

Article

Hysteretic Tricolor Electrochromic Systems Based on the Dynamic Redox Properties of Unsymmetrically Substituted Dihydrophenanthrenes and Biphenyl-2,2'-Diyl Dications: Efficient Precursor Synthesis by a Flow Microreactor Method

Yusuke Ishigaki ¹, Takanori Suzuki ^{1,*}, Jun-ichi Nishida ^{1,†}, Aiichiro Nagaki ², Naofumi Takabayashi ², Hidetoshi Kawai ^{1,‡}, Kenshu Fujiwara ¹ and Jun-ichi Yoshida ²

¹ Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan; E-Mails: y_ishigaki@mail.sci.hokudai.ac.jp (Y.I.); jnishida@echem.titech.ac.jp (J.N.); kawaih@rs.tus.ac.jp (H.K.); fjwkn@sci.hokudai.ac.jp (K.F.)

² Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 615-8530, Japan; E-Mails: anagaki@sbchem.kyoto-u.ac.jp (A.N.); tak@mail.sci.hokudai.ac.jp (N.T.); yoshida@sbchem.kyoto-u.ac.jp (J.Y.)

[†] Present address: Interdisciplinary School of Science and Engineering, Tokyo Institute of Technology, Yokohama 226-8502, Japan

[‡] Present address: Department of Chemistry, Faculty of Science, Tokyo University of Science, Shinjuku 162-8601, Japan

* Author to whom correspondence should be addressed; E-Mail: tak@sci.hokudai.ac.jp; Tel./Fax: +81-11-706-2714.

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Abstract: A series of biphenyl-2,2'-diylbis(diarylmethanol)s **3**, which have two kinds of aryl groups at the bay region, were efficiently obtained by integrated flow microreactor synthesis. The diols **3NO/NX** are the precursors of unsymmetric biphenylic dications **2NO/NX²⁺**, which are transformed into the corresponding dihydrophenanthrenes **1NO/NX** via **2NO/NX⁺** upon reduction, when they exhibit two-stage color changes. On the other hand, the steady-state concentration of the intermediate **2NO/NX⁺** is negligible during the oxidation of **1NO/NX** to **2NO/NX²⁺**, which reflects unique tricolor electrochromicity with a hysteretic pattern of color change [color 1→color 2→color 3→color 1].

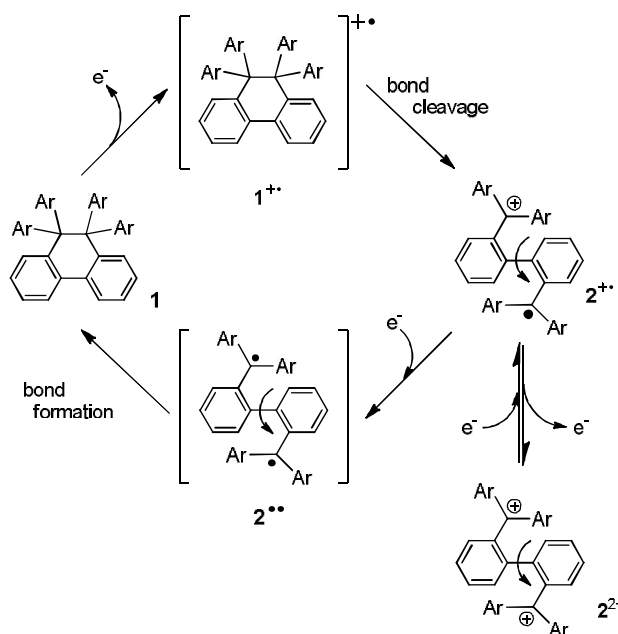
Keywords: electrochromism; organic dye; cationic dye; hysteresis; dynamic redox system; reaction integration; flow microreactor

1. Introduction

Electrochromism [1] is a representative function of organic redox systems, by which electrochemical input is reversibly transduced into UV-Vis spectral output. A vivid color change is a desirable feature of these systems, and thus the stable cationic dye moieties such as triarylmethyliums [2] have often been adopted for this purpose. During the course of our studies on “dynamic redox systems” [3,4] that undergo reversible C–C bond-formation/-breaking upon electron transfer, we found that 9,9,10,10-tetraaryl-9,10-dihydrophenanthrenes (DHP) **1** and biphenyl-2,2'-diylbis(diarylmethylium)s **2**²⁺ constitute a novel series of electrochromic pairs.

For example, the electron-donating DHPs (**1NN**, **1OO**, **1XX**) show absorptions only in the UV region, whereas the corresponding dications exhibit characteristic vivid colors (blue, red, or yellow) depending on the aryl group [$\lambda_{\text{max}}/\text{nm}$ (log ϵ) in MeCN: 661 (4.92), 604 (5.05) for **2NN**²⁺; 539sh (4.72), 514 (4.87) for **2OO**²⁺; 495sh (3.62) 460 (3.79) for **2XX**²⁺] [5,6]. Mechanistic studies have indicated that interconversion proceeds via the biphenyl-2,2'-diyl-type cation radical **2**^{•+} as a common intermediate (Scheme 1) [6,7]. For the C₂-symmetric derivatives shown above, however, this cation radical intermediate cannot be detected during the oxidation process of **1**, since **2**^{•+} is more easily oxidized than **1** [$E^{\text{ox}}(\mathbf{1}) > E^{\text{ox}}(\mathbf{2}^{\bullet+})$]. The same intermediate **2**^{•+} is also short-lived during the reduction of **2**²⁺, since **2**^{•+} undergoes facile disproportionation [$E_1^{\text{red}}(\mathbf{2}^{\bullet+}) \sim E_2^{\text{red}}(\mathbf{2}^{\bullet+})$] into **2**²⁺ and **2**^{••}, the latter of which is instantaneously converted to **1** by intramolecular C–C bond-formation. In this way, two-color switching [color 1 (**1**) $\rightleftharpoons$ color 2 (**2**²⁺)] is induced upon the application of electrochemical input to redox pairs with C₂-symmetry.

Scheme 1. Mechanism of interconversion between **1** and **2**²⁺.



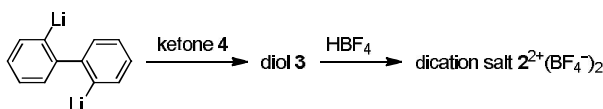
We envisaged that the proper molecular design could incorporate the intermediate 2^{++} in a novel tricolor electrochromism: disproportionation of 2^{++} to 2^{2+} and 2^{+} could be suppressed by attaching two kinds of aryl groups with different electron-donating properties. In this report we describe the preparation and novel electrochromic behavior of unsymmetrically substituted pairs such as $1NO/2NO^{2+}$ or $1NX/2NX^{2+}$. Flow microreactor synthesis [8-19] was very effective for sequentially attaching two different diarylmethyl units to the biphenyl skeleton, whereas the conventional macro batch method gave the desired products in low yields (ca. 10%). The color changes show hysteresis, in that there is a difference between oxidation [color 1 (**1**)→color 2 (2^{2+})] and reduction [color 2 (2^{2+})→color 3 (2^{+})→color 1 (**1**)].

2. Results and Discussion

2.1. Preparation of Unsymmetrically Substituted Diol-Precursors

Biphenyl-2,2'-diylbis(diarylmethanol)s **3** are the precursors of dicationic dyes 2^{2+} [5]. Diols with *C*₂-symmetry were readily obtained by reacting diarylketone **4** and 2,2'-dilithiobiphenyl, the latter of which was generated *in situ* from 2,2'-dihalobiphenyl and 2 equiv. of BuLi at -78°C (Scheme 2) [20]. To prepare unsymmetric diols **3NO** or **3NX** with two different diarylmethane units, we first used a mixture of two diarylketones (**4N-4O**, **4N-4X**) as an electrophile. Though the desired unsymmetric diols were obtained as a mixture containing two symmetric diols and other byproducts, tedious chromatographic separation only afforded pure **3NO** or **3NX** in respective yield of 12% and 9% [6]. Attempts to improve the yield were unfruitful even when dihalobiphenyl was treated sequentially with BuLi (1 equiv.), diarylketone (1 equiv.), BuLi (another 1 equiv.), and another diarylketone (1 equiv.). Again, a mixture of three diols was obtained, since selective monolithiation is difficult under the conventional macro batch conditions even if 1 equiv. of BuLi is used [21].

Scheme 2. Preparation of precursor diols **3** under the macro batch conditions.



On the other hand, some of us recently demonstrated that monolithiation of dibromobiphenyl can be successfully conducted under the flow microreactor conditions [22,23]. By taking advantage of this process, we succeeded in the sequential introduction of two diarylmethyl units by reaction integration using flow microreactor synthesis [24-26] (Figure 1) thanks to fast micromixing and precise temperature control. The best result was obtained when 0.1 M 2,2'-dibromobiphenyl in THF (flow rate 6.0 mL/min) was reacted with 0.5 M BuLi in hexane (1.2 mL/min) for 0.06 s at 24°C to generate 2-lithio-2'-bromobiphenyl, which was sequentially reacted with ketone **4O** (0.2 M in THF, 3.0 mL/min), BuLi (0.5 M in hexane, 1.44 mL/min), and another ketone **4N** (0.1 M in THF, 7.2 mL/min). This sequence of reactions proceeded in a short period of 15.5 s, and, unsymmetric diol **3NO** with 4-dimethylaminophenyl and 4-methoxyphenyl groups was generated in high NMR yield of 92% and isolated in 73% yield after chromatography. Under similar conditions, **3NX** with 4-dimethylaminophenyl and xanthenyl groups was prepared in 81% NMR yield and isolated in 61% yield.

Scheme 3. Formula of compounds

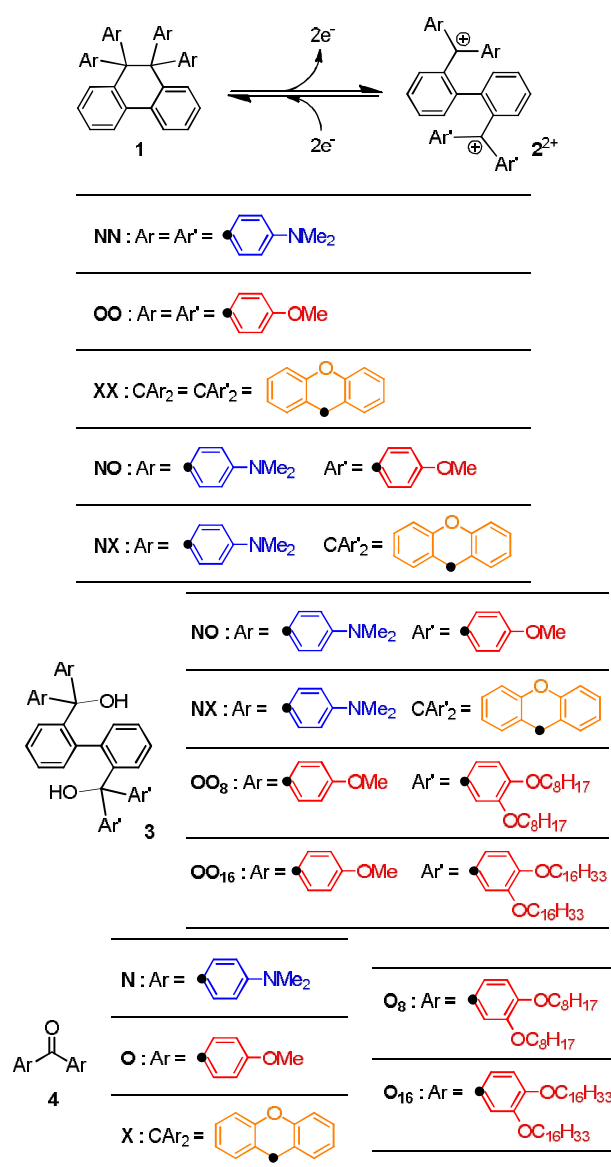
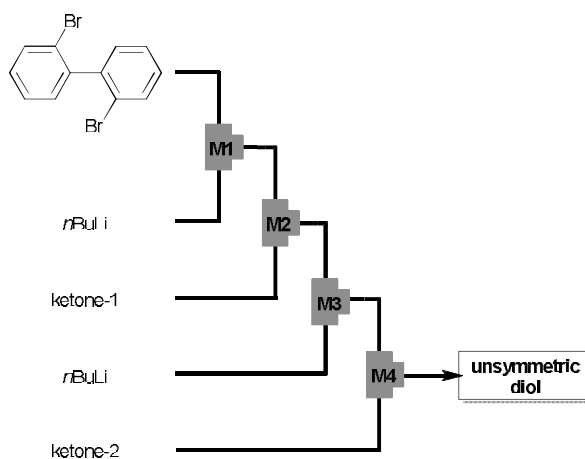


Figure 1. An integrated flow microreactor system for the sequential introduction of two different diarylmethanol units at the 2,2'-position of biphenyl.



In both **3NO** and **3NX**, the two diarylmethyl units differ significantly in terms of their electron-donating properties, so that the combination would be suitable for suppressing the disproportionation of the cation radical intermediate (**2NO^{•+}** and **2NX^{•+}**) during the electrochemical interconversion of **1** and **2²⁺**. In addition to its value in preparing the precursors of tricolor electrochromic systems shown above, the flow microreactor method can also produce another group of materials by adopting other bulky diarylketones with long alkoxy chains as an electrophile [e.g., 3,3',4,4'-tetrakis(octyloxy)- or tetrakis(hexadecyloxy)benzophenones, **4O₈** or **4O₁₆**]. Unsymmetrically substituted diols **3OO₈** and **3OO₁₆** were obtained in good isolated yields of 68% and 62%, respectively, and could be used to generate unique dicationic dyes that are soluble in a hydrocarbon solvent [7]. The results shown above clearly demonstrate that the flow microreactor system is very effective for the sequential introduction of two bulky substituents at the bay region of the biphenyl skeleton.

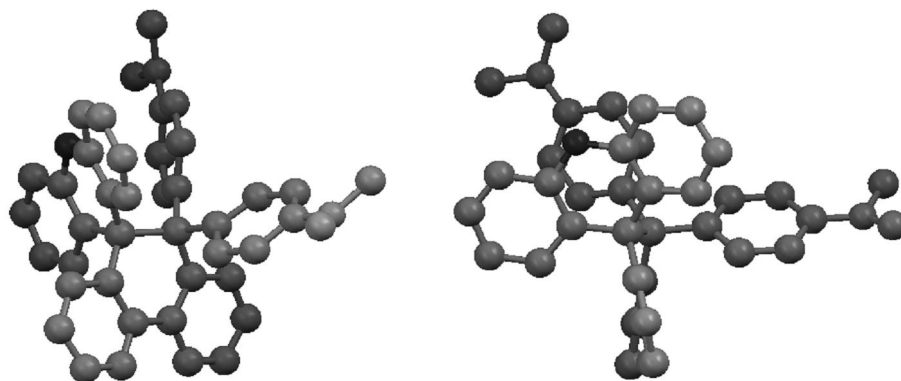
2.2. Preparation and Two-Electron Interconversion of Unsymmetrically Substituted Redox Pairs

When diols **3NO** and **3NX** were treated with $\text{HBF}_4\text{-(EtCO)}_2\text{O}$, deeply colored dications were isolated as stable BF_4^- salts in respective yields of 91 and 93%. In the UV-Vis spectrum of **2NO²⁺**(BF_4^-)₂ [$\lambda_{\text{max}}/\text{nm}$ (log ϵ) in MeCN: 632 (4.93), 519 (4.72)], both of the strong absorptions that are characteristic of two different triarylmethyl cations are present. Thus, the deep purple color of **2NO²⁺**(BF_4^-)₂ solution is due to the simple combination of blue and red chromophores found in **2NN²⁺** and **2OO²⁺**. Similarly, the green color of **2NX²⁺**(BF_4^-)₂ [632 (4.92), 488 sh (3.76), 425 (4.22)] can be accounted for by the presence of the blue and yellow dye units within the molecule.

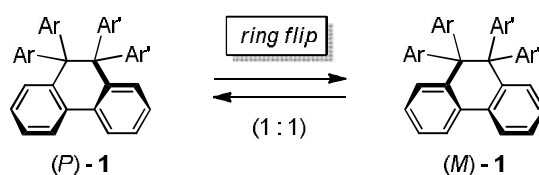
These dications were cleanly converted into colorless DHPs, **1NO** and **1NX**, upon reduction with SmI_2 in THF in respective yields of 97 and 78%. The resulting DHPs were reoxidized to **2NO²⁺** and **2NX²⁺** by treatment with 2 equiv. of (4- BrC_6H_4)₃ $\text{N}^+\text{SbCl}_6^-$ in CH_2Cl_2 , which were in turn isolated as deeply colored SbCl_6^- salts in respective yields of 82 and 79%. This high-yield interconversion indicates that **1NO/2NO²⁺** and **1NX/2NX²⁺** constitute a “reversible” redox pair although C–C bond-formation/-breaking is accompanied by electron transfer (“dynamic” redox behavior) [3,4].

According to an X-ray analysis of **1NX** (Figure 2), the C9–C10 bond of the DHP unit [1.643(6) Å] is longer than standard (1.54 Å) [27], which is due to the “front strain” [28] among the aryl groups at C9 and C10, as in the case of other polyarylated cyclic compounds [29–32]. The DHP skeleton adopts a half-chair conformation with a dihedral angle of 16.2° for two benzene nuclei, which endows the molecule with an asymmetric element of helicity (*P/M*). In a single crystal of **1NX** (space group: $P2_12_12_1$), all of the molecules adopt the same helicity, which shows that spontaneous resolution occurs. Based on the result of a VT-NMR experiment, however, the spectrum indicates *C*₁-symmetry only at low temperature (*N*-methyl protons: 2.95 and 2.80 ppm in CDCl_3), and *C*_s symmetry is attained at room temperature (*T*_c = −40 °C). *P/M*-**1NX** readily undergoes racemization due to facile ring-flip in solution ($\Delta G^\ddagger = 11.4 \text{ kcal mol}^{-1}$ at −40 °C) (Scheme 4), while this process is prohibited in the crystal.

Figure 2. Molecular structure of **1NX** determined by X-ray analysis: **(left)** top view; **(right)** side view. The DHP skeleton adopts a helical geometry, and all of the molecules in a single crystal are homochiral in terms of helicity.



Scheme 4. Interconversion of the enantiomers of helical DHPs **1** by ring flip.



2.3. Hysteretic Redox Behavior of Unsymmetrically Substituted Redox Pairs

The cyclic voltammograms of C_2 -symmetric DHPs are similar to each other, with an irreversible 2e-oxidation peak at +0.77 (**1NN**), +1.47 (**1OO**) or +1.42 (**1XX**) V vs. SCE in CH_2Cl_2 , respectively [5,6]. The return wave is largely shifted to the cathode, and was assigned to the 2e-reduction peak of 2NN^{2+} (−0.45 V), 2OO^{2+} (+0.18 V), or 2XX^{2+} (+0.50 V), respectively (Table 1). Similarly, the present unsymmetric DHPs **1NO** and **1NX** undergo irreversible 2e-oxidation (Figure 3). Their oxidation potentials are close to that of **1NN**, indicating that the HOMO level of **1NO** or **1NX** is close to that of **1NN** due to the dimethylaminophenyl groups with strong electron-donating properties. The irreversibility of the oxidation wave suggests that the as-generated cation radical, $1\text{NO}^{+\bullet}$ or $1\text{NX}^{+\bullet}$, readily isomerizes to $2\text{NO}^{+\bullet}$ or $2\text{NX}^{+\bullet}$ by C9–C10 bond fission. In the return cycle of the voltammogram of **1NO** or **1NX**, two cathodic peaks were seen: such behavior is quite different from that of C_2 -symmetric compounds.

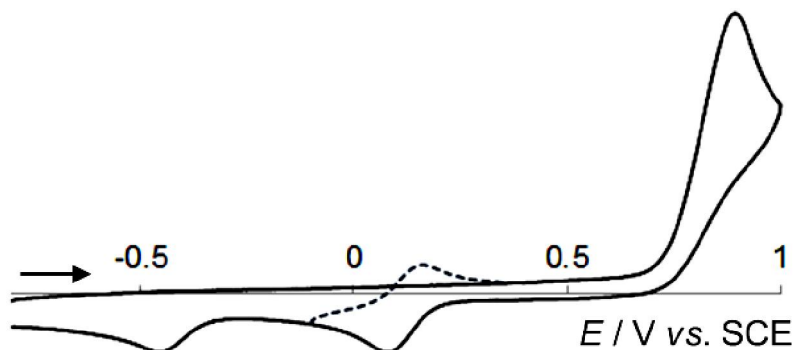
Table 1. Redox potentials of **1** and 2^{2+} in CH_2Cl_2 ^a.

compd.	E^{ox} (1)	E_1^{red} (2^{2+})	E_2^{red} (2^{2+})
NO	+0.83 ^{b,c}	+0.10 ^c	−0.45 ^c
NX	+0.76 ^{b,c}	+0.24 ^c	−0.19 ^c
NN	+0.74 ^{b,c}	−0.42 ^{b,c}	
OO	+1.44 ^{b,c}	+0.21 ^{b,c}	
XX	+1.39 ^{b,c}	+0.53 ^{b,c}	

^a E/V vs. SCE, 0.1 M Bu_4NBF_4 , Pt electrode, scan rate 100 mV/s; ^b Two-electron process;

^c Irreversible wave, values are calculated. as $E^{\text{ox}} = E_{\text{peak}} - 0.03$ and $E^{\text{red}} = E_{\text{peak}} + 0.03$.

Figure 3. Cyclic voltammogram of DHP **1NO** (10^{-3} M) in CH_2Cl_2 (E/V vs. SCE 0.1 M Bu_4NBF_4 , Pt electrode, scan rate 500 mV s^{-1}). The reduction peaks are absent when the voltammogram is first scanned cathodically. As shown by the dotted line, the first reduction wave at $+0.07$ V is reversible when the scanning is reversed at -0.10 V.

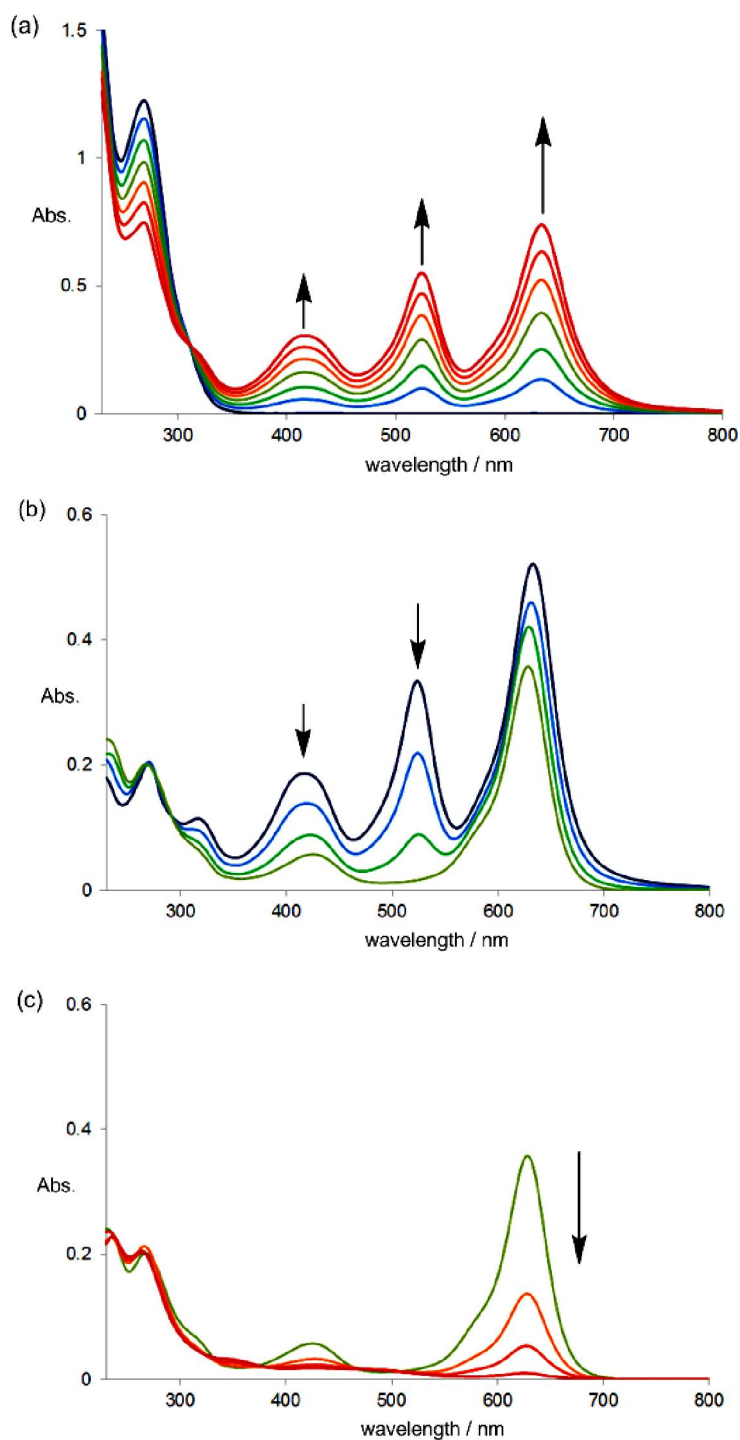


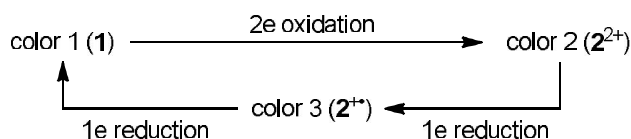
Independent measurements of 2NO^{2+} and 2NX^{2+} confirmed that the two cathodic peaks are due to two-stage 1e-reduction processes of the unsymmetric dication. The first process is completely reversible, and corresponds to the reduction of bis(4-methoxyphenyl)methyl cation in 2NO^{2+} or the xanthylium moiety in 2NX^{2+} . Furthermore, after scanning of the irreversible second 1e-reduction wave of 2NO^{2+} and 2NX^{2+} , the anodic peak due to the oxidation of **1NO** or **1NX** appears in the far anodic region of the voltammograms. Such redox properties can only be accounted for by assuming the reaction mechanism shown in Scheme 1, where the elongated C9–C10 bond in DHP is cleaved after just 1e oxidation of **1NO** to 1NO^{+} [33] whereas two-fold 1e-reduction of 2NO^{2+} to $2\text{NO}^{\bullet+}$ is necessary before the ring closure. $2\text{NO}^{\bullet+}$ produced from 1NO^{+} is more easily oxidized than **1NO** [$E^{\text{ox}}(\text{1NO}) = +0.83 \text{ V}$; $E^{\text{ox}}(2\text{NO}^{\bullet+}) = E_1^{\text{red}}(2\text{NO}^{2+}) = +0.10 \text{ V}$], and thus the steady-state concentration of $2\text{NO}^{\bullet+}$ is negligible during the electrochemical oxidation of **1NO**, although the same specimen is a long-lived intermediate in the reduction of 2NO^{2+} due to suppression of disproportionation. The same is true for another series of compounds, $1\text{NX}^{+}/1\text{NX}^{\bullet+}/2\text{NX}^{+}/2\text{NX}^{2+}$ [$E^{\text{ox}}(\text{1NX}) = +0.76 \text{ V}$; $E^{\text{ox}}(2\text{NX}^{\bullet+}) = E_1^{\text{red}}(2\text{NX}^{2+}) = +0.24 \text{ V}$; $E_2^{\text{red}}(2\text{NX}^{2+}) = -0.19 \text{ V}$]. Thanks to the hysteretic interconversion in redox reactions, unique tricolor electrochromic systems could be constructed using the present unsymmetric derivatives, as shown below.

2.4. Hysteretic Tricolor Electrochromicity of Unsymmetrically Substituted Redox Pairs

Upon the electrochemical oxidation of colorless **1NO** in CH_2Cl_2 , both the blue and red chromophores grow simultaneously to develop a violet color for 2NO^{2+} (Figure 4(a), isosbestic point at 310 nm). On the other hand, the red chromophore predominantly disappears in the first stage of the electrochemical reduction of 2NO^{2+} (Figure 4(b), 295 nm), and the blue cation radical $2\text{NO}^{\bullet+}$ is then converted to colorless **1NO** (Figure 4(c), 290 nm) even under constant-current electrolytic conditions (Scheme 5). A similar behavior, but with different colors, was observed for the xanthene derivative. Thus, colorless donor **1NX** was transformed directly into green 2NX^{2+} (isosbestic point: 309 nm), whereas reduction is a two-stage process; *i.e.*, green 2NX^{2+} changes to blue $2\text{NX}^{\bullet+}$ (248, 270, 300 nm) and blue $2\text{NX}^{\bullet+}$ changes to colorless **1NX** (296 nm), which shows the generality of the unique pattern of the color change.

Figure 4. Changes in the UV–VIS spectra of (a) **1NO** (3.5 mL; 3.0×10^{-5} M in CH_2Cl_2 containing 0.05 M Bu_4NBF_4) upon electrochemical oxidation (10 μA) at 5-min intervals, and **2NO²⁺** (3.5 mL soln; 6.2×10^{-6} M in CH_2Cl_2 containing 0.05 M Bu_4NBF_4) upon electrochemical reduction (40 μA): (b) stage 1, at 2-min intervals; (c) stage 2, at 8-min intervals.

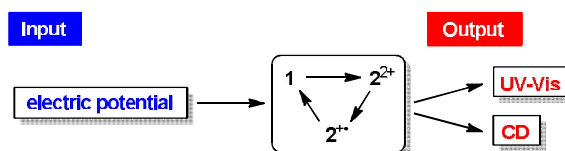
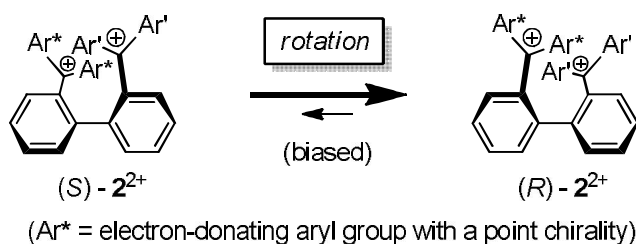


Scheme 5. Hysteretic color changes in the novel tricolor chromic systems.

3. Conclusions

Compared with the successful examples based on the polymeric materials [34-46], tricolor electrochromicity based on discrete molecules is rare, for which only a limited number of examples have been reported [47-51]. Even among successful examples, a hysteretic pattern for the color change, where there is a difference between oxidation [color 1→color 2] and reduction [color 2→color 3→color 1], is quite unique for the present systems. This novel chromicity is attained by the incorporation of biphenyldiyl-type cation radical $2^{\bullet+}$ as an additional component to DHP **1** and dication 2^{2+} . The key to extending the lifetime of $2^{\bullet+}$ is the different electron-donating properties of two dye chromophores, whose precursors were prepared very efficiently using the flow microreactor method.

We are now developing a new series of tricolor chromic system, which also afford chiroptical properties (e.g., circular dichroism (CD)) as an additional signal, to construct the multi-output response systems (Scheme 6) [3,4,7,52-54]. While the triarylmethyliums attached with chiral substituents only exhibit very small ellipticity to be used as an output signal ($|\Delta\epsilon| < 1.5$), huge enhancement ($|\Delta\epsilon| > 100$) could be realized by intramolecular transfer of the point chirality to the axial chirality in the biphenyl-diyl dications 2^{2+} (Scheme 7) [54], in which the two triarylmethylium units are suitably arranged for effective exciton coupling [52,53]. Studies along this vein are now in progress and the results will be reported in due course.

Scheme 6. Multi-output response based on the novel tricolor chromic systems.**Scheme 7.** Interconversion of the enantiomers of axially chiral dications 2^{2+} by rotation to give a diastomerically biased mixture due to the transfer of point chirality to axial chirality.

4. Experimental Section

4.1. Preparation of 9,9-Bis(4-Dimethylaminophenyl)-10,10-Bis(4-Methoxyphenyl)-9,10-Dihydrophenanthrene **1NO**

To a suspension of dication salt of **2NO**²⁺(BF₄[−])₂ (104 mg, 0.129 mmol) in THF (10 mL) was added triethylamine (3 mL) followed by SmI₂ (0.1 mol dm^{−3} in THF, 5.0 mL, 0.50 mmol) over 10 min at rt. The violet suspension gradually turned to ocher, and then the blue color of SmI₂ remained persistent during the addition. After stirring for 1 h and removal of THF and amine, the residue was suspended in water and extracted with benzene. The organic layer was washed with water and brine, and dried over K₂CO₃. Evaporation of solvent followed by chromatographic separation (Al₂O₃, benzene) gave DHP **1NO** as a colorless solid (79 mg, y. 97%).

Mp 284.5–285.5 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, 0 °C) δ/ppm 7.65–7.71 (2H, m), 7.18–7.25 (2H, m), 7.08–7.18 (4H, m), 6.80–7.06 (8H, m), 6.43–6.55 (4H, AA'XX'), 6.26–6.38 (4H, AA'XX'), 3.71 (6H, s), 2.85 (12H, s); IR (KBr) 2948, 2832, 1610, 1510, 1444, 1354, 1292, 1252, 1186, 1036, 950, 806, 746, 580 cm^{−1}; FD-MS *m/z* 630 (M⁺, BP); Anal. Calcd. for C₄₄H₄₂N₂O₂: C, 83.78; H, 6.71; N, 4.44. Found: C, 83.72; H, 6.88; N, 4.48.

4.2. Preparation of Spiro[10,10-Bis(4-Dimethylaminophenyl)-9,10-Dihydrophenanthrene-9,9'-[9H]Xanthene] **1NX**

To a suspension of **2NX**²⁺(BF₄[−])₂ (30 mg, 39.6 μmol) in THF (10 mL) was added SmI₂ (0.1 mol dm^{−3} in THF, 1.7 mL, 0.17 mmol) over 5 min at rt. The deep green suspension gradually turned to colorless during the addition. After stirring for 30 min and evaporation of THF, the residue was suspended in water and extracted with CH₂Cl₂. The organic layer was washed with water and brine, and dried over Na₂SO₄. Evaporation of solvent followed by separation by preparative TLC (SiO₂, hexane/AcOEt = 4) gave DHP **1NX** as a colorless solid (18 mg, y. 78%). Single crystalline specimen of **1NX** was obtained by recrystallization from ether.

Mp 294–295 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, 24 °C) δ/ppm 8.03 (1H, d, *J* = 7.8 Hz), 7.90 (1H, d, *J* = 7.8 Hz), 7.46 (1H, ddd, *J* = 7.8, 7.8, 1.5 Hz), 7.34 (1H, dd, *J* = 7.8, 1.5 Hz), 7.22–7.30 (3H, m), 7.13–7.19 (2H, m), 6.88–7.05 (3H, m), 6.63–6.72 (6H, m), 6.61 (2H, dd, *J* = 7.8, 1.5 Hz), 6.24 (4H, AA'XX'), 2.84 (12H, s); IR (KBr) 2796, 1610, 1518, 1480, 1440, 1354, 1312, 1244, 950, 808, 750 cm^{−1}; FD-MS *m/z* 584 (M⁺, BP); Anal. Calcd. for C₄₂H₃₆N₂O: C, 86.27; H, 6.21; N, 4.79. Found: C, 86.04; H, 6.41; N, 4.65.

4.3. Preparation of Biphenyl-2-yl[Bis(4-Dimethylaminophenyl)Methylum]-2'-yl[Bis(4'-Methoxyphenyl)Methylum] Bis(Tetrafluoroborate) **2NO**²⁺(BF₄[−])₂

To a solution of diol **3NO** (117 mg, 0.176 mmol) in DME (3 mL) was added propionic anhydride (0.6 mL) followed by 42% HBF₄ (6.70 M, 90 μL, 0.60 mmol), and the mixture was heated at 80 °C for 1 h. By slow cooling to rt, dication salt **2NO**²⁺(BF₄[−])₂ was separated as a deep-violet solid (129 mg, y. 91%), which was filtered, washed with DME and dried in vacuo.

Mp 194–198 °C (decomp.); ^1H NMR (400 MHz, CD_3CN , 20 °C) δ /ppm 7.00–7.70 (16H, m), 6.92–6.98 (4H, AA'XX'), 6.62–6.73 (4H, AA'XX'), 4.03 (3H, s), 4.02 (3H, s), 3.22 (6H, s), 3.17 (6H, s); IR (KBr) 1580, 1506, 1464, 1372, 1278, 1220, 1160, 1124, 1084, 1062, 938, 912, 838, 722 cm^{-1} ; FAB-MS m/z 630 (M^+ , BP); Anal. Calcd. for $\text{C}_{44}\text{H}_{42}\text{N}_2\text{O}_2\text{B}_2\text{F}_8 + 0.5\text{H}_2\text{O}$: C, 64.96; H, 5.33; N, 3.44. Found: C, 65.06; H, 5.40; N, 3.40.

4.4. Preparation of Biphenyl-2-yl[Bis(4-Dimethylaminophenyl)Methylium]-2'-yl[9-Xanthenylium] Bis(Tetrafluoroborate) $2\text{NX}^{2+}(\text{BF}_4^-)_2$

To a solution of diol **3NX** (70 mg, 11.3 μmol) in DME (3 mL) was added propionic anhydride (0.5 mL) followed by 42% HBF_4 (50 μL , 33.5 μmol), and the mixture was heated at 80 °C for 1 h. By slow cooling to rt, dication salt $2\text{NX}^{2+}(\text{BF}_4^-)_2$ was separated as a deep-green solid (80 mg, y. 93%), which was filtered, washed with DME, and dried in vacuo.

Mp 219–220 °C (decomp.); ^1H NMR (400 MHz, CD_3CN , 50 °C) δ /ppm 8.40 (2H, br.), 8.23 (2H, br. d, $J = 8.5$ Hz), 7.90 (2H, br. d, $J = 8.5$ Hz), 7.78–7.84 (3H, br. m), 7.46–7.56 (3H, br. m), 7.32 (2H, ddd, $J = 7.8, 7.8, 1.0$ Hz), 7.26–7.30 (1H, br. m), 6.85 (2H, br. d, $J = 7.8$ Hz), 6.20–7.20 (7H, br.), 3.30 (6H, br. s), 3.29 (6H, br. s); IR (KBr) 1622, 1584, 1506, 1374, 1174, 1084, 1036, 910, 762, 722 cm^{-1} ; FAB-MS m/z 584 (M^+ , BP); Anal. Calcd. for $\text{C}_{42}\text{H}_{36}\text{N}_2\text{OB}_2\text{F}_8$: C, 66.52; H, 4.78; N, 3.69. Found: C, 66.64; H, 4.79; N, 3.76.

4.5. Oxidation to Biphenyl-2-yl[Bis(4-Dimethylaminophenyl)Methylium]-2'-yl[Bis(4'-Methoxyphenyl)Methylium] Bis(Hexachloroantimonate) $2\text{NO}^{2+}(\text{SbCl}_6^-)_2$

To a solution of DHP **1NO** (10 mg, 15.9 μmol) in CH_2Cl_2 (10 mL) was added $(4\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ (26 mg, 31.8 μmol), and mixture was stirred for 20 min at rt. Deep-violet precipitates of $2\text{NO}^{2+}(\text{SbCl}_6^-)_2$ (17 mg, y. 82%) were separated upon dilution with hexane (1 mL), which were filtered, washed with CH_2Cl_2 and dried in vacuo.

Mp >310 °C (decomp.); IR (KBr) 1580, 1438, 1372, 1280, 1160, 1004, 938, 912, 832, 722, 578 cm^{-1} ; Anal. Calcd. for $\text{C}_{44}\text{H}_{42}\text{N}_2\text{O}_2\text{Sb}_2\text{Cl}_{12}$: C, 40.66; H, 3.26; N, 2.16. Found: C, 40.76; H, 3.29; N, 2.26.

4.6. Oxidation to Biphenyl-2-yl[Bis(4-Dimethylaminophenyl)Methylium]-2'-yl[9-Xanthenylium] Bis(Hexachloroantimonate) $2\text{NX}^{2+}(\text{SbCl}_6^-)_2$

To a solution of DHP **1NX** (5.0 mg, 8.6 μmol) in CH_2Cl_2 (2.5 mL) was added $(4\text{-BrC}_6\text{H}_4)_3\text{N}^+\text{SbCl}_6^-$ (14 mg, 17 μmol), and mixture was stirred for 10 min at rt. Deep-green precipitates of $2\text{NX}^{2+}(\text{SbCl}_6^-)_2$ (8.5 mg, y. 79%) were separated upon dilution with hexane (1 mL), which were filtered, washed with CH_2Cl_2 and dried in vacuo.

Mp 203–210 °C (decomp.); IR (KBr) 1620, 1582, 1504, 1476, 1372, 1168, 940, 910, 832, 754, 722 cm^{-1} ; Anal. Calcd. for $\text{C}_{42}\text{H}_{36}\text{N}_2\text{OSb}_2\text{Cl}_{12}$: C, 40.17; H, 2.89; N, 2.23. Found: C, 39.90; H, 3.05; N, 2.07.

4.7. Preparation of 2-[Bis(4-Dimethylaminophenyl)Hydroxymethyl]-2'-[Bis(4'-Methoxyphenyl)Hydroxymethyl]Biphenyl **3NO** via Flow Microreactor Method

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3, and M4), four microtube reactors (R1, R2, R3, and R4), and five microtube units [P1 (inner diameter $\phi = 1000\ \mu\text{m}$, length $l = 100\ \text{cm}$), P2 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$), P3 ($\phi = 1000\ \mu\text{m}$, $l = 100\ \text{cm}$), P4 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$), and P5 ($\phi = 1000\ \mu\text{m}$, $l = 100\ \text{cm}$)] was used. The whole flow microreactor system was dipped in a water bath (24 °C). A solution of 2,2'-dibromobiphenyl (0.10 M) in THF (flow rate = 6.00 mL min⁻¹) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min⁻¹) were introduced to M1 ($\phi = 250\ \mu\text{m}$). The resulting solution was passed through R1 ($\phi = 500\ \mu\text{m}$, $l = 3.5\ \text{cm}$) and was mixed with a solution of 4,4'-dimethoxybenzophenone **4O** (0.20 M) in THF (flow rate = 3.00 mL min⁻¹) in M2 ($\phi = 500\ \mu\text{m}$). The resulting solution was passed through R2 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$) and was introduced to M3 ($\phi = 500\ \mu\text{m}$) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min⁻¹). The resulting solution was passed through R3 ($\phi = 1000\ \mu\text{m}$, $l = 200\ \text{cm}$) and was introduced to M4 ($\phi = 500\ \mu\text{m}$) where the solution was mixed with a solution of 4,4'-bis(dimethylamino)benzophenone **4N** (0.10 M) in THF (flow rate = 7.20 mL min⁻¹). The resulting solution was passed through R4 ($\phi = 1000\ \mu\text{m}$, $l = 200\ \text{cm}$). After a steady state was reached, the product solution was collected for 60 s and was treated with BuLi (1.67 M) in hexane (2.0 mL) to consume excess ketones and quench the reaction with water.

After diluted with H₂O, the whole mixture was extracted with Et₂O. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 3) to give **3NO** (291 mg) as a colorless solid in 73% yield.

Mp 221–222 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, 24 °C) δ /ppm 7.00–7.10 (9H, m), 6.92–6.96 (2H, br. d, $J = 8.8\ \text{Hz}$), 6.74–6.86 (9H, m), 6.61–6.65 (4H, m), 6.19 (1H, dd, $J = 8.6, 1.0\ \text{Hz}$), 6.04 (1H, dd, $J = 8.6, 1.0\ \text{Hz}$), 5.23 (1H, s), 3.83 (3H, s), 3.78 (3H, s), 3.56 (1H, s), 2.95 (6H, s), 2.91 (6H, s); IR (KBr) 3550sh, 2900, 2832, 1612, 1512, 1466, 1352, 1298, 1250, 1174, 1062, 826, 762, 560 cm⁻¹; FD-MS m/z (rel intensity) 664 (M^+ , 100), 646 (3); Anal. Calcd. for C₄₄H₄₄N₂O₄: C, 79.49; H, 6.67; N, 4.21. Found: C, 79.37; H, 6.80; N, 4.05.

4.8. Preparation of 2-[Bis(4-Dimethylaminophenyl)Hydroxymethyl]-2'-[Bis(4'-Methoxyphenyl)Hydroxymethyl]Biphenyl **3NO** via Macro Batch Method

To a colorless solution of 2,2'-diiodobiphenyl (692 g, 1.70 mmol) in THF (12 mL) was added dropwise BuLi (1.70 mol dm⁻³ in hexane, 2.30 mL, 3.91 mmol) at -78 °C for 5 min under Ar, and the mixture was stirred for 45 min at this temperature. To the resultant suspension of 2,2'-dilithiobiphenyl was added a mixture of 4,4'-bis(dimethylamino)benzophenone **4N** (406 mg, 1.51 mmol) and 4,4'-dimethoxybenzophenone **4O** (364 mg, 1.50 mmol) in THF (30 mL) for 15 min. After stirring for 4 h, BuLi (1.70 mol dm⁻³ in hexane, 1.00 mL, 1.70 mmol) was added for 3 min to consume excess ketones. The resultant red solution was further stirred for 1 h and quenched by adding water. THF was evaporated, and the residue was extracted with benzene. The organic layer was washed with water and brine, and dried over Na₂SO₄. Evaporation of the solvent gave 1.09 g of oily material containing

unsymmetric diol **3NO**. Two symmetric diols, **3NN** and **3OO**, were also formed in this reaction. Chromatographic separation on SiO₂ (hexane/AcOEt = 7/3) followed by crystallization from ether gave **3NO** as colorless crystals (120 mg, y. 12%).

4.9. Preparation of 9-[2'-Bis(4-Dimethylaminophenyl)Hydroxymethylbiphenyl-2-yl]-9-Hydroxyxanthene **3NX** via Flow Microreactor Method

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3, and M4), four microtube reactors (R1, R2, R3, and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μ m, length l = 100 cm), P2 (ϕ = 1000 μ m, l = 50 cm), P3 (ϕ = 1000 μ m, l = 100 cm), P4 (ϕ = 1000 μ m, l = 50 cm), and P5 (ϕ = 1000 μ m, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bath (24 °C). A solution of 2,2'-dibromobiphenyl (0.10 M) in THF (flow rate = 6.00 mL min⁻¹) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min⁻¹) were introduced to M1 (ϕ = 250 μ m). The resulting solution was passed through R1 (ϕ = 500 μ m, l = 3.5 cm) and was mixed with a solution of xanthone **4X** (0.20 M) in THF (flow rate = 3.00 mL min⁻¹) in M2 (ϕ = 500 μ m). The resulting solution was passed through R2 (ϕ = 1000 μ m, l = 50 cm) and was introduced to M3 (ϕ = 500 μ m) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min⁻¹). The resulting solution was passed through R3 (ϕ = 1000 μ m, l = 200 cm) and was introduced to M4 (ϕ = 500 μ m) where the solution was mixed with a solution of 4,4'-bis(dimethylamino)benzophenone **4N** (0.10 M) in THF (flow rate = 7.20 mL min⁻¹). The resulting solution was passed through R4 (ϕ = 1000 μ m, l = 200 cm). After a steady state was reached, the product solution was collected for 60 s and was treated with BuLi (1.67 M) in hexane (2.0 mL) to consume excess ketones and quench the reaction with water. After diluted with H₂O, the whole mixture was extracted with Et₂O. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5) to give **3NX** (227 mg) as a colorless solid in 61% yield.

Mp 143–152 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, 24 °C) δ /ppm 7.63 (1H, dd, J = 7.8, 1.5 Hz), 7.39 (1H, dd, J = 7.8, 1.5 Hz), 7.32 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 7.09–7.24 (6H, m), 7.02 (2H, AA'XX'), 6.95–7.00 (2H, m), 6.87 (2H, AA'XX'), 6.83–6.93 (3H, m), 6.72 (1H, ddd, J = 7.8, 7.8, 1.5 Hz), 6.64 (2H, AA'XX'), 6.59 (2H, AA'XX'), 6.18 (1H, dd, J = 7.8, 1.5 Hz), 5.72 (1H, m), 3.02 (1H, s), 2.94 (6H, s), 2.93 (6H, s); IR (KBr) 3048, 2796, 1612, 1520, 1478, 1450, 1354, 1240, 1190, 1154, 1032, 948, 816, 758 cm⁻¹; FD-MS m/z 618 (M⁺, 100); Anal. Calcd. for C₄₂H₃₈N₂O₃: C, 81.53; H, 6.19; N, 4.53. Found: C, 81.60; H, 6.19; N, 4.40.

4.9. Preparation of 9-[2'-Bis(4-Dimethylaminophenyl)Hydroxymethylbiphenyl-2-yl]-9-Hydroxyxanthene **3NX** via Macro Batch Method

To a colorless solution of 2,2'-diiodobiphenyl (2.04 g, 5.02 mmol) in THF (20 mL) was added dropwise BuLi (1.47 mol dm⁻³ in hexane, 7.10 mL, 10.4 mmol) at 0 °C under Ar, and the mixture was stirred for 10 min at this temperature. To the resultant suspension of 2,2'-dilithiobiphenyl was added a mixture of 4,4'-bis(dimethylamino)benzophenone **4N** (1.30 g, 4.85 mmol) and xanthone **4X** (971 mg, 4.95 mmol) in THF (90 mL). After stirring for 2h at rt, the reaction was quenched by adding water.

THF was evaporated, and the residue was extracted with benzene. The organic layer was washed with water and brine, and dried over Na₂SO₄. Evaporation of the solvent gave 3.66 g of oily material containing unsymmetric diol **3NX**. Two symmetric diols, **3NN** and **3XX**, were also formed in this reaction. Chromatographic separation on SiO₂ (AcOEt/hexane, 1/4–1/2) followed by crystallization from MeOH gave **3NX** as colorless crystals (250 mg, y. 8.6%).

4.10. Preparation of 2-{Bis[3,4-Bis(Octyloxy)Phenyl]Hydroxymethyl}-2'-[Bis(4'-Methoxyphenyl)Hydroxymethyl]Biphenyl **300₈**

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3, and M4), four microtube reactors (R1, R2, R3, and R4), and five microtube units [P1 (inner diameter ϕ = 1000 μ m, length l = 100 cm), P2 (ϕ = 1000 μ m, l = 50 cm), P3 (ϕ = 1000 μ m, l = 100 cm), P4 (ϕ = 1000 μ m, l = 50 cm), and P5 (ϕ = 1000 μ m, l = 100 cm)] was used. The whole flow microreactor system was dipped in a water bath (24 °C). A solution of 2,2'-dibromobiphenyl (0.10 M) in THF (flow rate = 6.00 mL min⁻¹) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min⁻¹) were introduced to M1 (ϕ = 250 μ m). The resulting solution was passed through R1 (ϕ = 500 μ m, l = 3.5 cm) and was mixed with a solution of 4,4'-dimethoxybenzophenone **4O** (0.20 M) in THF (flow rate = 3.00 mL min⁻¹) in M2 (ϕ = 500 μ m). The resulting solution was passed through R2 (ϕ = 1000 μ m, l = 50 cm) and was introduced to M3 (ϕ = 500 μ m) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min⁻¹). The resulting solution was passed through R3 (ϕ = 1000 μ m, l = 200 cm) and was introduced to M4 (ϕ = 500 μ m) where the solution was mixed with a solution of 3,3',4,4'-tetrakis(octyloxy)benzophenone **4O₈** (0.10 M) in THF (flow rate = 7.20 mL min⁻¹). The resulting solution was passed through R4 (ϕ = 1000 μ m, l = 200 cm). After a steady state was reached, the product solution was collected for 120 s and was treated with H₂O to quench the reaction.

After diluted with H₂O, the whole mixture was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 3) to give **300₈** (889 mg) as a colorless oil in 68% yield.

¹H NMR (300 MHz, CDCl₃) δ /ppm 7.11–7.00 (6H, m), 6.85–6.72 (12H, m), 6.62 (1H, dd, J = 8.4, 1.8 Hz), 6.52 (1H, dd, J = 8.4, 1.8 Hz), 6.14–6.08 (2H, m), 4.39 (1H, s), 4.19 (1H, s), 4.00 (2H, t, J = 6.6 Hz), 3.97 (2H, t, J = 6.6 Hz), 3.90–3.74 (10H, m), 1.89–1.63 (8H, m), 1.53–1.18 (40H, m), 0.94–0.82 (12H, m); ¹³C NMR (100 MHz, CDCl₃) δ /ppm 158.53, 158.45, 148.35, 148.31, 148.26, 147.75, 143.94, 143.87, 141.12, 140.88, 138.98, 138.80, 131.58, 131.33, 130.31, 130.18, 129.64, 128.53, 125.98, 125.93, 125.79, 121.16, 120.34, 115.04, 113.10, 112.97, 112.87, 112.57, 83.35, 83.17, 69.27, 69.20, 69.12, 68.95, 55.18, 55.15, 31.78, 29.41, 29.35, 29.23, 29.13, 25.98, 25.94, 22.62, 14.05; IR (neat) 3538, 3397, 3053, 2953, 2927, 2856, 1607, 1583, 1509, 1468, 1442, 1435, 1417, 1379, 1298, 1252, 1175, 1162, 1137, 1064, 1037, 1064, 1037, 828, 808, 789, 756 cm⁻¹; FD-MS m/z 1091 (M⁺, 83), 1090 (BP); FD-HR-MS (FD) Calcd. for C₇₂H₉₈O₈: 1090.7262 Found: 1090.7244.

4.11. Preparation of 2-{Bis[3,4-Bis(Hexadecyloxy)Phenyl]Hydroxymethyl}-2'-[Bis(4'-Methoxyphenyl)Hydroxymethyl]Biphenyl **300₁₆**

An integrated flow microreactor system consisting of four T-shaped micromixers (M1, M2, M3, and M4), four microtube reactors (R1, R2, R3, and R4), and five microtube units [P1 (inner diameter $\phi = 1000\ \mu\text{m}$, length $l = 100\ \text{cm}$), P2 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$), P3 ($\phi = 1000\ \mu\text{m}$, $l = 100\ \text{cm}$), P4 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$), and P5 ($\phi = 1000\ \mu\text{m}$, $l = 100\ \text{cm}$)] was used. The whole flow microreactor system was dipped in a water bath (24 °C). A solution of 2,2'-dibromobiphenyl (0.10 M) in THF (flow rate = 6.00 mL min⁻¹) and a solution of BuLi (0.50 M) in hexane (flow rate = 1.20 mL min⁻¹) were introduced to M1 ($\phi = 250\ \mu\text{m}$). The resulting solution was passed through R1 ($\phi = 500\ \mu\text{m}$, $l = 3.5\ \text{cm}$) and was mixed with a solution of 4,4'-dimethoxybenzophenone **40** (0.20 M) in THF (flow rate = 3.00 mL min⁻¹) in M2 ($\phi = 500\ \mu\text{m}$). The resulting solution was passed through R2 ($\phi = 1000\ \mu\text{m}$, $l = 50\ \text{cm}$) and was introduced to M3 ($\phi = 500\ \mu\text{m}$) where the solution was mixed with a solution of BuLi (0.50 M) in hexane (flow rate = 1.44 mL min⁻¹). The resulting solution was passed through R3 ($\phi = 1000\ \mu\text{m}$, $l = 200\ \text{cm}$) and was introduced to M4 ($\phi = 500\ \mu\text{m}$) where the solution was mixed with a solution of 3,3',4,4'-tetrakis(hexadecyloxy)benzophenone **40₁₆** (0.10 M) in toluene (flow rate = 7.20 mL min⁻¹). The resulting solution was passed through R4 ($\phi = 1000\ \mu\text{m}$, $l = 200\ \text{cm}$). After a steady state was reached, the product solution was collected for 60 s and was treated with H₂O to quench the reaction.

After diluted with H₂O, the whole mixture was extracted with CH₂Cl₂. The combined organic layers were washed with water and brine, and dried over anhydrous Na₂SO₄. After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (CH₂Cl₂/hexane = 2) and GPC separation (1+2H) to give **300₁₆** (889 mg) as a colorless oil in 68% yield, which was solidified upon standing.

Mp 60–62 °C; ¹H NMR (300 MHz, CDCl₃) δ /ppm 7.11–6.99 (6H, m), 6.85–6.72 (12H, m), 6.63 (1H, dd, $J = 8.4, 1.8\ \text{Hz}$), 6.52 (1H, dd, $J = 8.4, 1.8\ \text{Hz}$), 6.14–6.08 (2H, m), 4.39 (1H, s), 4.19 (1H, s), 4.00 (2H, t, $J = 6.6\ \text{Hz}$), 3.96 (2H, t, $J = 6.6\ \text{Hz}$), 3.90–3.73 (10H, m), 1.89–1.62 (8H, m), 1.52–1.18 (104H, m), 0.92–0.82 (12H, m); ¹³C NMR (100 MHz, CDCl₃) δ /ppm 158.56, 158.50, 148.40, 148.36, 148.28, 147.79, 143.97, 143.90, 141.16, 140.91, 140.65, 139.02, 138.85, 131.61, 131.36, 130.34, 130.21, 129.67, 128.57, 126.02, 125.97, 125.85, 121.20, 120.37, 115.11, 113.15, 113.00, 112.92, 112.62, 83.38, 83.20, 69.32, 69.25, 69.17, 69.02, 55.23, 55.20, 31.92, 29.71, 29.66, 29.51, 29.46, 29.37, 29.30, 29.20, 26.06, 26.02, 25.99, 22.68, 14.10; IR (KBr) 3382, 3051, 2919, 2850, 1607, 1510, 1468, 1434, 1416, 1389, 1302, 1254, 1173, 1138, 1064, 1039, 827, 810, 760, 721, 560 cm⁻¹; FD-MS m/z 1540 (BP), 1539 (M⁺, 82); FD-HR-MS (FD) Calcd. for C₁₀₄H₁₆₂O₈: 1539.2270 Found: 1539.2297.

4.12. Preparation of 3,3',4,4'-Tetrakis(Octyloxy)Benzophenone **40₈**

To a solution of 4-bromo-1,2-bis(octyloxy)benzene (4.14 g, 10.0 mmol) in 50 mL of dry ether was added BuLi in hexane (1.57 M, 6.40 mL, 10.0 mmol) at 22 °C under Ar, and the mixture was stirred for 1 h. To the suspension was added *N*-carboethoxypiperidine (770 μL , 4.99 mmol) and the mixture was stirred at 23 °C for 20 h. After diluted with 3 M HCl aq., the whole mixture was extracted with CH₂Cl₂. The combined organic layers were washed with 3 M HCl aq. and 1 M NaOH aq., and dried

over anhydrous MgSO_4 . After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2$) to give **4O₈** (2.92 g) as a colorless solid in 84% yield.

Mp 58.5–59.5 °C; ^1H NMR (300 MHz, CDCl_3) δ /ppm 7.40 (2H, d, $J = 1.8$ Hz), 7.35 (2H, dd, $J = 8.4, 1.8$ Hz), 6.88 (2H, d, $J = 8.4$ Hz), 4.07 (4H, t, $J = 6.6$ Hz), 4.04 (4H, t, $J = 6.6$ Hz), 1.93–1.77 (8H, m), 1.55–1.21 (40H, m), 0.93–0.82 (12H, m); ^{13}C NMR (100 MHz, CDCl_3) δ /ppm 194.63, 152.74, 148.64, 130.69, 124.67, 114.65, 111.50, 69.28, 69.07, 31.82, 29.35, 29.27, 29.20, 29.10, 25.99, 22.67, 14.10; IR (KBr) 2955, 2920, 2873, 2852, 1665, 1597, 1581, 1518, 1469, 1413, 1390, 1343, 1301, 1265, 1237, 1200, 1127, 1023, 1011, 964, 847, 821, 753, 721, 626 cm^{-1} ; FD-MS m/z 695 (M^+ , BP); Anal. Calcd. for $\text{C}_{45}\text{H}_{74}\text{O}_5$: C, 77.76; H, 10.73. Found: C, 77.76; H, 10.71%.

4.13. Preparation of 3,3',4,4'-Tetrakis(Hexadecyloxy)Benzophenone **4O₁₆**

To a solution of 4-bromo-1,2-bis(hexadecyloxy)benzene (5.01 g, 7.85 mmol) in 25 mL of dry ether and 25 mL of dry hexane was added BuLi in hexane (1.57 M, 5.00 mL, 7.85 mmol) at 23 °C under Ar, and the mixture was stirred for 1 h. To the suspension was added *N*-carboethoxypiperidine (600 μL , 3.89 mmol) and the mixture was stirred at 24 °C for 23 h. After diluted with 3 M HCl aq., the whole mixture was extracted with CH_2Cl_2 . The combined organic layers were washed with 3 M HCl aq. and 1 M NaOH aq., and dried over anhydrous MgSO_4 . After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{hexane} = 1$) to give **4O₁₆** (3.56 g) as a colorless solid in 80% yield.

Mp 81.5–83.0 °C; ^1H NMR (300 MHz, CDCl_3) δ /ppm 7.40 (2H, d, $J = 1.8$ Hz), 7.34 (2H, dd, $J = 8.4, 1.8$ Hz), 6.88 (2H, d, $J = 8.4$ Hz), 4.07 (4H, t, $J = 6.6$ Hz), 4.03 (4H, t, $J = 6.6$ Hz), 1.92–1.76 (8H, m), 1.53–1.18 (104H, m), 0.92–0.82 (12H, m); ^{13}C NMR (100 MHz, CDCl_3) δ /ppm 194.61, 152.74, 148.64, 130.69, 124.67, 114.65, 111.49, 69.28, 69.07, 31.93, 29.71, 29.64, 29.43, 29.37, 29.20, 29.12, 26.01, 22.68, 14.11; IR (KBr) 2956, 2917, 2849, 1661, 1597, 1579, 1518, 1468, 1432, 1414, 1392, 1342, 1266, 1237, 1200, 1125, 1030, 1016, 850, 754, 721, 625 cm^{-1} ; FD-MS m/z 1143 (M^+ , BP); Anal. Calcd. for $\text{C}_{77}\text{H}_{138}\text{O}_5$: C, 80.85; H, 12.16. Found: C, 80.73; H, 12.15%.

4.14. Preparation of 4-Bromo-1,2-Bis(Hexadecyloxy)Benzene

To a solution of 1,2-bis(hexadecyloxy)benzene (14.9 g, 26.7 mmol) in 200 mL of dry CH_2Cl_2 was added *N*-bromosuccinimide (4.75 g, 26.7 mmol) in dry MeCN 70 mL at 23 °C under Ar, and the mixture was stirred for 20 h. After diluted with water, the whole mixture was extracted with CH_2Cl_2 . The combined organic layers were washed with 10% $\text{Na}_2\text{S}_2\text{O}_3$ aq. and brine, and dried over anhydrous MgSO_4 . After filtration, solvent was concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 200 to 100) to give 4-bromo-1,2-bis(hexadecyloxy)benzene (16.8 g) as a colorless solid in 99% yield.

Mp 62.5–63.5 °C; ^1H NMR (300 MHz, CDCl_3) δ /ppm 7.00–6.94 (2H, m), 6.72 (1H, d, $J = 9.1$ Hz), 3.95 (2H, t, $J = 6.6$ Hz), 3.94 (2H, t, $J = 6.6$ Hz), 1.86–1.72 (4H, m), 1.52–1.17 (52H, m), 0.92–0.84 (6H, m); ^{13}C NMR (100 MHz, CDCl_3) δ /ppm 150.06, 148.38, 123.42, 116.95, 115.17, 112.79, 69.53, 69.38, 31.93, 29.71, 29.63, 29.38, 29.23, 29.13, 25.99, 22.70, 14.11; IR (KBr) 2917, 2848, 1588, 1509, 1503, 1468, 1446, 1434, 1392, 1324, 1258, 1220, 1132, 1066, 1014, 955, 865, 842, 826, 800, 722, 644,

576 cm^{-1} ; FD-MS m/z (relative intensity) 638 (M^+ , 35), 636 (M^+ , 35), 559 (BP); Anal. Calcd. for $\text{C}_{38}\text{H}_{69}\text{O}_2\text{Br}$: C, 71.55; H, 10.90. Found: C, 71.37; H, 10.80%.

4.15. Measurement of Redox Potentials

All the redox potentials (E^{ox} and E^{red}) were measured under argon atmosphere by cyclic voltammetry in CH_2Cl_2 containing 0.1 M Bu_4NBF_4 as a supporting electrolyte. All the values are reported in E/V vs. SCE, and Pt wire was used as the working electrode. In the case of irreversible waves, half-wave potentials were estimated from the peak potentials as $E^{\text{ox}} = E^{\text{pa}}$ (anodic peak potential) -0.03 V, and $E^{\text{red}} = E^{\text{pc}}$ (cathodic peak potential) $+0.03$ V.

4.16. X-Ray Structural Analyses

Unsymmetric DHP **1NX**: $\text{C}_{42}\text{H}_{36}\text{N}_2\text{O}$, M 584.76, $0.60 \times 0.10 \times 0.05$ mm, orthorhombic, space group $P2_12_12_1$, $a = 10.4511(4)$, $b = 14.0601(7)$, $c = 20.771(1)$ Å, $V = 3052.2(3)$ Å³ [3,4], and D_{calcd} ($Z = 4$) = 1.272 g cm^{-3} . Numerical absorption correction was applied ($\mu = 0.76 \text{ cm}^{-1}$). Data collection was performed on a Rigaku Mercury CCD camera apparatus (Mo- $\text{K}\alpha$ radiation, $\lambda = 0.71069$ Å, 50 kV, 50 mA) at 203 K. The structure was solved by the direct method and refined by full-matrix least-squares method on F with anisotropic temperature factors for non-hydrogen atoms. Hydrogen atoms were located at the calculated positions. The final R and R_w values are 0.044 and 0.049 for 407 parameters and 2835 reflections with $I > 3\sigma(I)$ (independent reflections, 3625; $2\theta_{\text{max}} = 53.5^\circ$). The GOF indicator is 1.20. Residual electron density is 0.16 Å^{-3} . CCDC 182/1003

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References

1. Monk, P.M.S.; Mortimer, R.J.; Rosseinsky, D.R. *Electrochromism and Electrochromic Devices*; Cambridge University Press: Cambridge, MA, USA and New York, NY, USA, 2007.
2. Muthyala, R. *Chemistry and Application of Leuco Dyes*; Plenum Press: New York, NY, USA and London, UK, 1997.
3. Suzuki, T.; Higuchi, H.; Tsuji, T.; Nishida, J.; Yamashita, Y.; Miyashi, T. *Chemistry of Nanomolecular Systems. Chapter 1: Dynamic Redox Systems*; Nakamura, T., Matsumoto, T., Tada, T., Sugiura, K., Eds.; Springer: Heidelberg, Germany, 2003; pp. 3-24.
4. Suzuki, T.; Ohta, E.; Kawai, H.; Fujiwara, K.; Fukushima, T. Dynamic redox systems as electrochromic materials: Bistability and advanced response. *Synlett (Account)* **2007**, *38*, 851-869.
5. Suzuki, T.; Nishida, J.; Tsuji, T. Hexaphenylethane derivatives exhibiting novel electrochromic behavior. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1329-1331.
6. Suzuki, T.; Nishida, J.; Tsuji, T. A new type of tricolor electrochromic system based on the dynamic redox properties of hexaarylethane derivatives. *Chem. Commun.* **1998**, *20*, 2193-2194.

7. Suzuki, T.; Ishigaki, Y.; Iwai, T.; Kawai, H.; Fujiwara, K.; Ikeda, H.; Kano, Y.; Mizuno, K. Multi-input/multi-output molecular response system based on the dynamic redox behavior of 3,3,4,4-tetraaryldihydro[5]helicene derivatives: Reversible formation/destruction of chiral fluorophore and modulation of chiroptical properties by solvent polarity. *Chem. Eur. J.* **2009**, *15*, 9434-9441.
8. Jähnisch, K.; Hessel, V.; Löwe, H.; Baerns, M. Chemistry in microstructured reactors. *Angew. Chem. Int. Ed.* **2004**, *43*, 406-446.
9. Doku, G.N.; Verboom, W.; Reinhoudt, D.N.; van den Berg, A. On-microchip multiphase chemistry—A review of microreactor design principles and reagent contacting modes. *Tetrahedron* **2005**, *61*, 2733-2742.
10. Watts, P.; Haswell, S.J. The application of micro reactors for organic synthesis. *Chem. Soc. Rev.* **2005**, *34*, 235-246.
11. Yoshida, J. Flash chemistry using electrochemical method and microsystems. *Chem. Commun.* **2005**, *36*, 4509-4516.
12. Geyer, K.; Codee, J.D.C.; Seeberger, P.H. Microreactors as tools for synthetic chemists—The chemists' round-bottomed flask of the 21st century? *Chem. Eur. J.* **2006**, *12*, 8434-8442.
13. De Mello, A.J. Control and detection of chemical reactions in microfluidic systems. *Nature* **2006**, *442*, 394-402.
14. Song, H.; Chen, D.L.; Ismagilov, R.F. Reactions in droplets in microfluidic channels. *Angew. Chem. Int. Ed.* **2006**, *45*, 7336-7356.
15. Kobayashi, J.; Mori, Y.; Kobayashi, S. Multiphase organic synthesis in microchannel reactors. *Chem. Asian. J.* **2006**, *1*, 22-35.
16. Mason, B.P.; Price, K.E.; Steinbacher, J.L.; Bogdan, A.R.; McQuade, D.T. Greener approaches to organic synthesis using microreactor technology. *Chem. Rev.* **2007**, *107*, 2300-2318.
17. Ahmed-Omer, B.; Brandtand, J.C.; Wirth, T. Advanced organic synthesis using microreactor technology. *Org. Biomol. Chem.* **2007**, *5*, 733-740.
18. Fukuyama, T.; Rahman, M.T.; Sato, M.; Ryu, I. Adventures in inner space: Microflow systems for practical organic synthesis. *Synlett* **2008**, *2*, 151-163.
19. Yoshida, J.; Nagaki, A.; Yamada, T. Flash chemistry: Fast chemical synthesis by using microreactors. *Chem. Eur. J.* **2008**, *14*, 7450-7459.
20. Neugebauer, N.; Kos, A.J.; Schleyer, P.R. Regioselektive dimetallierung von aromaten. Bequemer zugang zu 2,2'-disubstituierten biphenylderivaten. *J. Organomet. Chem.* **1982**, *228*, 107-118.
21. Leroux, F.; Nicod, N.; Bonnafox, L.; Quissac, B.; Colobert, F. New vistas in halogen/metal exchange reactions: The discrimination between seemingly equal halogens. *Lett. Org. Chem.* **2006**, *3*, 165-169.
22. Nagaki, A.; Takabayashi, N.; Tomida, Y.; Yoshida, J. Selective monolithiation of dibromobiaryls using microflow systems. *Org. Lett.* **2008**, *10*, 3937-3940.
23. Nagaki, A.; Takabayashi, N.; Tomida, Y.; Yoshida, J. Synthesis of unsymmetrically substituted biaryls via sequential lithiation of dibromobiaryls using integrated microflow systems. *Beilstein J. Org. Chem.* **2009**, *5*, doi:10.3762/bjoc.5.16.

24. Usutani, H.; Tomida, Y.; Nagaki, A.; Okamoto, H.; Nokami, T.; Yoshida, J. Generation and reactions of *o*-bromophenyllithium without benzyne formation using a microreactor. *J. Am. Chem. Soc.* **2007**, *129*, 3046-3047.
25. Nagaki, A.; Tomida, Y.; Usutani, H.; Kim, H.; Takabayashi, N.; Nokami, T.; Okamoto, H.; Yoshida, J. Integrated micro flow synthesis based on sequential br–li exchange reactions of *p*-, *m*-, and *o*-dibromobenzenes. *Chem. Asian J.* **2007**, *2*, 1513-1523.
26. Suga, S.; Yamada, D.; Yoshida, J. Cationic three-component coupling involving an optically active enamine derivative. From time integration to space integration of reactions. *Chem. Lett.* **2010**, *39*, 404-406.
27. Allen, F.H.; Kennard, O.; Watson, D.G.; Brammer, L.; Orpen, A.G.; Taylor, R. Tables of bond lengths determined by X-ray and neutron diffraction. Part 1. Bond lengths in organic compounds. *J. Chem. Soc. Perkin Trans. 2* **1987**, *12*, S1-S19.
28. Kahr, B.; Engen, D.V.; Mislow, K. Length of the ethane bond in hexaphenylethane and its derivatives. *J. Am. Chem. Soc.* **1986**, *108*, 8305-8307.
29. Suzuki, T.; Takeda, T.; Kawai, H.; Suzuki, T. Ultralong C–C bonds in hexaphenylethane derivatives. *Pure Appl. Chem.* **2008**, *80*, 547-553.
30. Kawai, H.; Takeda, T.; Fujiwara, K.; Wakeshima, M.; Hinatsu, Y.; Suzuki, T. Ultralong carbon-carbon bonds in dispirobis(10-methylacridan) derivatives with an acenaphthene, pyracene, or dihydropyracylene skeleton. *Chem. Eur. J.* **2008**, *14*, 5780-5793.
31. Takeda, T.; Kawai, H.; Herges, R.; Mucke, E.; Sawai, Y.; Fujiwara, K.; Suzuki, T. Negligible diradical character for the ultralong C–C bond in 1,1,2,2-tetraarylpyracene derivatives at room temperature. *Tetrahedron Lett.* **2009**, *50*, 3693-3697.
32. Dyker, G.; Körning, J.; Bubenitschek, P.; Jones, P.G. Palladium-catalyzed synthesis of propellanes with hexaarylethane structure. *Liebigs Ann. Recl.* **1997**, *1*, 203-209.
33. Maslak, P.; Chapman, W.H., Jr.; Vallombroso, T.M., Jr.; Watson, B.A. Mesolytic Scission of C–C bonds in radical cations of amino derivatives: Steric and solvent effects. *J. Am. Chem. Soc.* **1995**, *117*, 12380-12389.
34. Huang, L.-T.; Yen, H.-J.; Chang, C.-W.; Liou, G.-S. Red, green, and blue electrochromism in ambipolar poly(amine-amide-imide)s based on electroactive tetraphenyl-*p*-phenylenediamine units. *J. Polymer Sci.* **2010**, *48*, 4747-4757.
35. Koyuncu, S.; Zafer, C.; Sefer, E.; Koyuncu, F.B.; Demic, S.; Kaya, I.; Ozdemir, E.; Icli, S. A new conducting polymer of 2,5-bis(2-thienyl)-1*H*-(pyrrole) (SNS) containing carbazole subunit: Electrochemical, optical and electrochromic properties. *Synth. Met.* **2009**, *159*, 2013-2021.
36. Zeng, Q.; McNally, A.; Keyes, T.E.; Forster, R.J. Redox induced switching dynamics of a three colour electrochromic metallopolymer film. *Electrochim. Acta* **2008**, *53*, 7033-7038.
37. Ozyurt, F.; Gunbas, E.G.; Durmus, A.; Toppare, L. Processable and multichromic polymer of bis-3-hexylthiophene substituted 4-*tert*-butylphenyl quinoxaline. *Org. Elect.* **2008**, *9*, 296-302.
38. Zeng, Q.; McNally, A.; Keyes, T.E.; Forster, R.J. Three colour electrochromic metallopolymer based on a ruthenium phenolate complex bound to poly(4-vinyl)pyridine. *Electrochem. Commun.* **2008**, *10*, 466-470.

39. Li, X.-G.; Wang, H.-Y.; Huang, M.-R. Synthesis, film-forming, and electronic properties of *o*-phenylenediamine copolymers displaying an uncommon tricolor. *Macromolecules* **2007**, *40*, 1489-1496.
40. Thompson, B.C.; Kim, Y.-G.; McCarley, T.D.; Reynolds, J.R. Soluble narrow band gap and blue propylenedioxythiophene-cyanovinylene polymers as multifunctional materials for photovoltaic and electrochromic applications. *J. Am. Chem. Soc.* **2006**, *128*, 12714-12725.
41. Sonmez, G.; Wudl, F. Completion of the three primary colours: The final step toward plastic displays. *J. Mat. Chem.* **2005**, *15*, 20-22.
42. Yano, J.; Yamasaki, S. Three-color electrochromism of an aramid film containing polyaniline and poly(*o*-phenylenediamine). *Synth. Met.* **1999**, *102*, 1157.
43. Sotzing, G.A.; Reddinger, J.L.; Katritzky, A.R.; Soloduch, J.; Musgrave, R.; Reynolds, J.R.; Steel, P.J. Multiply colored electrochromic carbazole-based polymers. *Chem. Mat.* **1997**, *9*, 1578-1587.
44. Yano, J.; Terayama, K.; Yamasaki, S. Electrochemically prepared poly(*o*-phenylenediamine)—Prussian blue composite film for a three-colour expressible ECD material. *J. Mat. Sci.* **1996**, *31*, 4785-4792.
45. Yamasaki, S.; Terayama, K.; Yano, J. Poly(*p*-phenylene terephthalamide) film immobilizing oligomer species as a colored matrix for three-color electrochromic displays. *J. Electrochem. Soc.* **1996**, *143*, L212-L214.
46. Yang, J.; Kai, S.; Ogura, K. Poly(*o*-phenylenediamine)-Prussian blue composite film for a three-colour-expressible electrochromic display material. *J. Mat. Sci. Lett.* **1993**, *12*, 1791-1792.
47. Sugimoto, T.; Nagatomi, T.; Ando, H.; Yoshida, Z. Redox-active thieno[3,2-*b*]thiophene as a novel, three-color electrochromic system. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 560-561.
48. Li, X.-G.; Wang, H.-Y.; Huang, M.-R. Synthesis, film-forming, and electronic properties of *o*-phenylenediamine copolymers displaying an uncommon tricolor. *Macromolecules* **2007**, *40*, 1489-1496.
49. Zeng, Q.; McNally, A.; Forster, R.J. Redox induced switching dynamics of a three colour electrochromic metallopolymer film. *Electrochem. Acta* **2008**, *53*, 7033-7038.
50. Deng, W.; Flood, A.H.; Stoddart, J.F.; Goddard, W.A., III. An electrochemical color-switchable rgb dye: Tristable [2]catenane. *J. Am. Chem. Soc.* **2005**, *127*, 15994-15995.
51. Ikeda, T.; Saha, S.; Aprahamian, I.; Leung, K.C.F.; Williams, A.; Deng, W.; Flood, A.H.; Goddard, W.A., III; Stoddart, J.F. Toward electrochemically controllable tristable three-station [2]catenanes. *Chem. Asian J.* **2007**, *2*, 76-93.
52. Nishida, J.; Suzuki, T.; Ohkita, M.; Tsuji, T. A redox switch based on dihydro[5]helicene: Drastic chiroptical response induced by reversible C—C bond making/breaking upon electron transfer. *Angew. Chem. Int. Ed.* **2001**, *40*, 3251-3254.
53. Suzuki, T.; Yamamoto, R.; Higuchi, H.; Hirota, E.; Ohkita, M.; Tsuji, T. Electrochiroptical response of a hexaarylethane derivative with a helical π -skeleton: Drastic UV-Vis and CD spectral changes upon electrolysis of 4',5'-dibromodispiro[xanthene-9,9'(9'*H*,10'*H*)-phenanthrene-10',9''-xanthene]. *J. Chem. Soc. Perkin Trans.* **2002**, *2*, 1937-1942.

54. Suzuki, T.; Iwai, T.; Ohta, E.; Kawai, H.; Fujiwara, K. Electrochiroptical systems based on biphenyl-2,2'-diyl-type dicationic dyes: Strong chiroptical signals through the transmission of point chirality to axial chirality. *Tetrahedron Lett.* **2007**, *48*, 3599-3603.

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