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# Donor-only substituted benzene achieves thermally activated delayed fluorescence

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Thermally activated delayed fluorescence (TADF) is a promising mechanism for harvesting triplet excitons in organic light-emitting diodes (OLEDs). The donor–acceptor (D–A) design is the most conventional strategy for developing efficient TADF emitters. A subsequently emerged approach, known as the multiple resonance (MR) effect, also employs electron-donating and electron-withdrawing functional groups. Thus, developing TADF materials has traditionally relied on ingenuity in selecting and combining two functional units. Here, we have realized a TADF molecule by utilizing only a carbazole donor moiety. This molecule is an unusual example in the family of TADF materials and offers better insight into the electronic structures in the excited states for luminescent materials.

Purely organic thermally activated delayed fluorescent (TADF) materials have been widely developed in the past decade primarily for use in organic light-emitting diodes (OLEDs)<sup>1</sup>. Exciton dynamics, including the triplet-tosinglet upconversion through reverse intersystem crossing (RISC), enables the harvesting of dark triplet excitons for high electroluminescence efficiencies in OLEDs<sup>2</sup>. In addition to the OLED application, the luminescent feature with long-lived delayed fluorescence, which is quenched by oxygen, makes TADF materials suitable for time-resolved imaging<sup>3</sup>. Further, TADF molecules have been employed in photocatalytic synthesis, photodynamic therapy, and X-ray imaging scintillators<sup>4-8</sup>. The most essential aspect of TADF materials is the small energy gap between the first singlet and triplet excited states (S<sub>1</sub> and T<sub>1</sub>) referred to as  $\Delta E_{ST}$ , which allows the electronic transitions with spin conversion. The fundamental design guideline for creating molecules with a small  $\Delta E_{ST}$  is understood by electron exchange integral K of the frontier molecular orbitals (FMOs) responsible for the transition<sup>9</sup>. The electron exchange interaction destabilizes the singlet states, while it stabilizes the triplet states, indicating that smaller K leads to smaller  $\Delta E_{\rm ST}$ . Thus, the smaller spatial overlap between FMOs of the transition, which are normally between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the smaller  $\Delta E_{ST}$ . A spatially separated HOMO and LUMO in a molecule is easily achieved in charge-transfer (CT)-type excited states. The molecules with electron donor (D) and electron acceptor (A) units strongly localise HOMO and LUMO on each unit, respectively, and induce the electron transfers from D to A in the excited states. Thus, D-A-based molecular design has played a pivotal role in developing TADF materials<sup>10-14</sup>. A typical D-A-type TADF molecule, **4CzIPN**, is shown in Fig. 1<sup>2</sup>. In general, the D and A units need a weak conjugation by increasing the dihedral angle or introducing a spacer unit between D-A units for better CT characteristics<sup>15-18</sup>. Another important class of molecular design is known as the multiple resonance (MR) effect, which realises short-range CT in the rigid  $\pi$ -conjugated framework as represented by the **DABNA** scaffold<sup>19-24</sup>. The alternating resonance effects by electron-donating and electronwithdrawing substituents in the ortho relation localise HOMO and LUMO at different carbon atoms in benzene rings. With few exceptions<sup>25-34</sup>, the TADF materials have been designed by D-A or MR strategies, indicating that electronically disparate building blocks are considered to be necessary. The classification of D and A is based on a relative scale and is sometimes complicated because of independent inductive and resonance effects as seen in halogen substitution on benzene ring. In 2020, the first example of TADF materials (DBF-DMAc) using the strong-D and weak-D units as the D-A system was reported by Tsuchiya et al.<sup>35</sup>. In 2022, Hall et al. reported an MR compound (DiICzMes<sub>4</sub>) without an electron withdrawing group and they described that MR-TADF with no acceptor groups is possible<sup>36</sup>, followed by several works using the same indolo[3,2,1-jk]carbazole (ICz) and similar indolo[3,2,1-de]acridine structures<sup>37-40</sup>. Interestingly, the ICz unit could be capable as an electron acceptor in the D-A type TADF materials (ICzAc)<sup>41</sup>. As mentioned above, a wide variety of TADF materials have provided a better understanding of electronic structures and excited state dynamics of TADF materials. Therefore, it is highly desired to expand molecular design by developing unexpected systems.

In this work, we demonstrate TADF from a simplified molecular structure with 3,6-dimethoxy-carbazole donor-only substituted benzene (6MeOCzPh, Fig. 1). We recently revealed that hexacarbazolylbenzene

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**Fig. 1** | **Examples of TADF molecules.** A typical D–A molecule **4CzIPN** has carbazole donors and isophthalonitrile acceptor. A typical MR molecule **DABNA1** has electron-donating nitrogen and electron-withdrawing boron atoms. Strong D–weak D act as D–A, respectively. Fused ICz derivatives show MR characteristics without the electron-withdrawing atom. ICz also acts as the acceptor unit against the strong donor for forming D–A. **6MeOC2Ph** developed in this work is an additional TADF

molecule without explicit acceptor moiety. Unconventional TADF materials are like neither D–A nor MR design, while the electronic structures of these molecules may follow these types; for example, **Eosin** may have MR effect and **TQB** showing excited state intramolecular proton transfer (ESIPT) forms CT excited states similar to D–A type. The n- $\pi^*$  transition observed in quinones, thiones, and TCA\_C4 also leads to the small spatial overlap of FMOs.



**Fig. 2** | **Photophysical properties of 6CzPh derivatives in solution. Inset: Chemical structures. a, b** Fluorescence (solid lines) and phosphorescence (dashed lines) spectra for **6CzPh, 6tBuCzPh**, and **6MeOCzPh** in toluene and chloroform,

respectively. **c-e** Transient PL decay curves of **6MeOCzPh** in toluene, chloroform, and DMF, respectively.

(6CzPh) is useful as the host molecule because of its high T<sub>1</sub> energy level and improvement of horizontal orientations of guest emitters<sup>42</sup>. Compared to 1,3-di(9-carbazolyl)benzene (mCP or m2CzPh), the  $\Delta E_{ST}$  value of 6CzPh was markedly reduced. Although 6CzPh does not show TADF, we further investigated a series of 6CzPh derivatives for potential TADF application. By increasing the donor strength of carbazole, the  $\Delta E_{ST}$  values were decreased to a sufficiently low level, exhibiting TADF in both solution and film states.

#### **Results and discussion**

The synthesis of 6CzPh derivatives having 3,6-di-*tert*-butylcarbazole and 3,6-dimethoxycarbazole (**6tBuCzPh** and **6MeOCzPh**, Fig. 2) followed the method for **6CzPh** by nucleophilic aromatic substitution ( $S_NAr$ ) reaction from hexafluorobenzene (Supplementary Methods S1). The impurities with unreacted fluorine atoms were removed by column chromatography and vacuum sublimation, and the absence of fluorine atoms was confirmed by

Table 1 | Photophysical characteristics of 6MeOCzPh in solution and blend films with PS and PMMA

Condition	λ <sub>PL</sub> [nm]	S <sub>1</sub> [eV]	T <sub>1</sub> [eV] <sup>a</sup>	∆ <i>E</i> <sub>ST</sub> [eV]	Ф <sub>РL</sub> [-] <sup>ь</sup>	Φ <sub>p</sub> /Φ <sub>d</sub> [-] <sup>ь</sup>	τ <sub>p</sub> [ns] <sup>b</sup>	τ <sub>d</sub> [μs] <sup>ь</sup>	<i>k</i> <sub>r</sub> [10 <sup>7</sup> s <sup>-1</sup> ]	<i>k</i> <sub>ISC</sub> [10 <sup>7</sup> s <sup>−1</sup> ]	<i>k</i> <sub>RISC</sub> [10 <sup>4</sup> s <sup>-1</sup> ]
In toluene	448	3.11	2.91	0.20	0.25	0.21/0.04	8.7	19	2.5	9.0	1.2
In chloroform	464	3.08	2.91	0.17	0.13	0.12/0.01	7.4	4.8	1.6	12	2.7
In acetone	478	3.04	2.91	0.13	0.16	0.14/0.02	9.2	7.9	1.5	9.4	2.2
In DMF	485	3.00	2.86	0.14	0.12	0.10/0.02	11	5.2	0.90	8.2	4.6
In PS <sup>c</sup>	444	3.14	2.85	0.29	0.11	0.09/0.02	4.2	31	2.2	22	0.63
In PMMA <sup>d</sup>	452	3.12	2.85	0.27	0.19	0.16/0.03	6.0	20	2.6	14	1.2

<sup>a</sup>Measured at 77 K.

<sup>b</sup>Measured under N<sub>2</sub> in solution or Ar in films.

°Polystyrene.

<sup>d</sup>Poly(methyl methacrylate).



Fig. 3 | Photophysical properties of 6MeOCzPh in polymethylmethacrylate (PMMA). a Fluorescence (blue line) and phosphorescence (green line) spectra. b Temperature dependence of transient PL decay curves. c Prompt and delayed emission spectra at room temperature.

<sup>19</sup>F NMR. A single crystal suitable for X-ray structure analysis was obtained for **6tBuCzPh** by sublimation and **6MeOCzPh** by recrystallization from chloroform and acetonitrile. Similar to **6CzPh**, the molecules have the C1 point group symmetry (Supplementary Fig. S1). Because of the rigid structures, 6CzPh derivatives did not melt in the standard melting point apparatus.

The photophysical properties of 6CzPh derivatives were first evaluated in toluene and chloroform. Photoluminescence (PL) spectra of 6CzPh at room temperature were broad and structureless, similar to CT-type emission (Fig. 2). The phosphorescence spectra measured at 77 K showed vibrational structures, which are closely related to the local triplet excited state of carbazole moiety. Since the  $T_1$  energies of **6CzPh** (~3.0 eV) were slightly decreased compared to those of carbazole (~3.1 eV), and vibrational bands of 6CzPh and carbazole are apparently different (Supplementary Fig. S2), the distributions of molecular orbitals extend through the intramolecular interactions. Because of the relatively high S<sub>1</sub> energy (>3.35 eV) with the emission maxima at about 400 nm, 6CzPh has  $\Delta E_{ST}$  values of >0.3 eV (Table S1) which are larger than the standard threshold (<0.2 eV) for TADF to be observed. The S1 energies of 6tBuCzPh with 3,6-di-tertbutylcarbazole (tBuCz) donors were slightly decreased, while the T1 energies of tBuCz were also decreased, keeping large  $\Delta E_{ST}$  values. On the other hand, the stronger donor of 3,6-dimethoxycarbazole showed much shifted S<sub>1</sub> to the lower energies. As a result, the  $\Delta E_{ST}$  of **6MeOCzPh** reached 0.2 eV in toluene (Table 1), and a very weak TADF was observed in time-resolved PL measurements. With increasing the solvent polarity, the delayed components became clear because of the smaller  $\Delta E_{ST}$  values (Fig. 2 and Supplementary Fig. S3-S4). The prompt and delayed emission in DMF showed typical temperature dependence behavior of TADF (Supplementary Fig. S5–S6)<sup>43</sup>, indicating that TADF from only donor-substituted benzene is possible.

The TADF properties were further characterized in doped thin-film states. A polystyrene (PS) film with 6 wt% doping of **6MeOCzPh** showed the emission maxima similar to that in toluene (Table 1). Because of the low polarity of PS, the  $\Delta E_{ST}$  and delayed lifetime ( $\tau_d$ ) were relatively large as with the results in toluene. The use of slightly polar poly(methyl methacrylate) (PMMA) hosts exhibited better results, although the spectra were essentially similar (Fig. 3 and Supplementary Fig. S7). The transient PL spectra revealed clear prompt and delayed components with the same spectra shape, supporting delayed fluorescence for emission in the microsecond range. The temperature dependence of the rate constants of RISC ( $k_{RISC}$ ), which follows the Arrhenius equation  $k_{RISC} = \exp(-\Delta E/k_bT)$  (Supplementary Fig. S8), indicated thermal activation of the process. These results also support the TADF in **6MeOCzPh**.

The distinctive aspect of the molecular and electronic structures behind the observation of TADF in 6MeOCzPh will be discussed below. Although the structure only includes 3,6-dimethoxycarbazole and benzene moieties, the broad emission spectra suggested the possibility of the CT-type excited state. Thus, the single benzene ring might behave as an acceptor. Although the LUMO level of benzene itself is much higher than that of carbazole (Fig. 4a), it decreases with an increasing the number of carbazole substituents because of the electron-withdrawing inductive effect of the nitrogen atoms (Supplementary Fig. S9). This effect is clearly observed in the <sup>13</sup>C NMR spectra exhibiting large downfield shifts of the carbon atoms connected to the carbazole moiety (Fig. 4b)<sup>44</sup>. As the result of the multiple substitutions, the LUMO level of 6CzPh is lower than that of carbazole and similar to that of benzonitrile. In addition, the non-bonding orbital interactions of nitrogen 2p orbitals with the p orbitals of the benzene  $\pi$ -system stabilized benzene  $\pi^*$  orbital energy. Thus, the LUMO is spreading over the central benzene ring and completely separated from the HOMO distributions (Fig. 4c). Although the inductive effects of tert-butyl and methoxy



**Fig. 4** | **Analysis of the electronic structures and intramolecular interactions. a** Calculated HOMO-LUMO energy levels at the B3LYP/6-31+G(d,p). **b** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra for **6CzPh** and fragment molecules. **c** HOMO and LUMO of

**6MeOCzPh. d** The reduced density gradient (RDG) isosurface map (iso value of 0.5) for **6CzPh. e** RDG scatter diagram for **6CzPh**.

substituted carbazoles seem to be similar (Supplementary Fig. S10), the strong donors shifted both HOMO and LUMO, and decreased energy gap, resulting in the realisation of the sufficiently close  $S_1$  level against the local  $T_1$  level. These results suggest that the D–A interactions cause the TADF property in **6MeOCzPh** despite the structure lacking an acceptor moiety. We sometimes overlook the negative inductive effect of the donor groups. Still, it has played an essential role as observed in the comparison between benzonitrile and **5CzBN** and must be carefully considered in the molecular designs.

We should also consider particular through-space intramolecular interactions and molecular orbital overlap with multiple carbazole rings tethered around the central benzene, which may form the threedimensional  $\pi$ -delocalization for loop electron migration<sup>45-48</sup>. Indeed, the S1 energy of 1,2,4,5-tetra(9-carbazolyl)benzene appeared at a much higher level than that of 6CzPh regardless of the linear decrease of the LUMO energies with increasing the number of carbazoles (Supplementary Fig. S11)<sup>49</sup>. Besides that, the fluorescence spectrum of **6CzPh** is already broad despite a relatively weak D-A interaction confirmed by the small solvatochromism of emission. The NMR peaks for carbazole rings in 6CzPh are markedly shifted from those in o2CzPh with the dicarbazole at the ortho position. In addition, the theoretical investigations visualised the non-covalent interactions between carbazole rings (Fig. 4d, e and Supplementary Fig. S12). The reduced density gradient (RDG) analysis exhibited intramolecular van der Waals interactions in green color<sup>50-52</sup>. The RDG isosurface map of 6CzPh indicated the intramolecular attractive interactions among hexad carbazoles to form toroidal  $\pi$ delocalization. As the co-facial  $\pi$ -interaction significantly affects the excited state energies, for example, commonly observed shifts of energy levels in the solid states, the intramolecular interactions in the donutshaped toroidal structure might contribute to a decrease in  $\Delta E_{ST}$  values. The molecular design considering three-dimensional interactions holds the potential for additional strategy to control excited-state characteristics in future material developments.

#### Conclusions

In this work, we have demonstrated TADF in the hexacarbazolylbenzene derivative. Apart from the standard strategy for developing TADF materials that combines two functional units, the molecular structure only includes carbazole-donor and benzene moieties without explicit electron-acceptor units. A single benzene substituted with the relatively strong donor units of 3,6-dimethoxy-carbazole, **6MeOCzPh**, exhibited typical TADF characteristics in both solution and film states. The physical insight of the molecular design is that the electron acceptor is induced by donor units. In addition, the toroidal  $\pi$ -delocalization by through space intramolecular interactions might have an impact on the excited states. These ideas would open new paths in luminophore developments and further study is expected to advance our understanding of excited state dynamics.

### Methods

## General

Commercially available materials for the synthesis were used as received from the suppliers. Details of instruments and physical measurements are given in Supplementary Note S1.

#### Synthesis and characterizations

The synthetic procedures and characterization data for each material are described in Supplementary Methods S1, and NMR and MS spectra are given in Supplementary Fig. S13–S18 and Fig. S19–S21, respectively.

#### X-ray single crystal analysis

X-ray crystallographic information files (CIFs) are available. CCDC 2369634–2369635 contain the supplementary crystallographic data for

this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data\_request/cif.

#### Theoretical calculations

The computations were mainly performed using the computer facilities at the Research Institute for Information Technology, Kyushu University. Molecular orbital calculations were performed using the program Gaussian 16. The geometries were optimized at the B3LYP/6-31+G(d,p) (Supplementary Table S2–S5). The natural population analysis (NPA) and natural bond orbital (NBO) analysis were calculated at the B3LYP/6-31+G(d,p) with NBO 7.0 program using optimized geometries<sup>51</sup>. The RDG analysis was performed on Multiwfn<sup>52,53</sup>, and plotted by VMD<sup>54</sup>.

## Data availability

The data that support the findings of this study are available in the supplementary material of this article. Source data are provided in Supplementary Data 1 with this paper. Additional information is available from the authors on request.

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## **Author contributions**

M.M. and C.A. conceptualized the research. M.M. and S.Y. synthesized and characterized the materials. M.M., S.Y., M.H., R.U., and H.K. performed the measurements and the data analysis. M.M. wrote the manuscript. M.M., T.H., and C.A. obtained the funding. All authors edited the manuscript.

# **Competing interests**

The authors declare no competing interests.

# **Additional information**

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