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Biphen[3]arenes based on V-shaped units: synthesis and macrocyclization-enhanced thermally activated delayed fluorescence†

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A new class of thermally activated delayed fluorescence (TADF) macrocycles is reported. Among them, cyclic trimers (biphen[3]arenes) based on V-shaped units were synthesized for the first time. And all trimeric macrocycles show macrocyclization-enhanced TADF, where the quantum yield greatly increased from 36.8% to 70.9%.

Organic luminescent macrocycles have recently emerged as promising tools for biological imaging,[1] chemical sensing[2] and optoelectronics[3] due to their distinct macrocyclic structures and interesting optical properties. Currently, there are two main strategies to construct macrocycles with luminescence. For macrocycles devoid of chromophores and remarkable conjugation, such as cyclodextrins,[4] cucurbiturils,[5] calixarenes[6] and pillararenes,[7] an effective method is introducing π-conjugated chromophores on their portals or side chains.[8] But this strategy is often accompanied by long synthetic steps and rather low yields. In contrast, using chromophores as both the macrocycle skeleton and the luminescent unit to construct luminescent macrocycles is a convenient and facile strategy. Based on this, a variety of organic luminescent macrocycles have been elaborately designed and efficiently synthesized, mainly including macrocyclic arenes[9] connected with methylene bridges and π-conjugated macrocycles.[10] The creative design and construction of luminescent macrocycles contributes to their versatility and utility in supramolecular chemistry and materials science. Furthermore, developing new luminescent macrocycles and studying the relationship between their structures and optical properties is important and meaningful for practical application in various scientific domains.

Macrocyclic arenes have attracted much attention due to their excellent molecular recognition and self-assembly properties.[11] In terms of the luminescence mechanism, luminescent macrocycles usually emit fluorescence or phosphorescence, while macrocycles with the emerging thermally activated delayed fluorescence (TADF) property remain scarce. Thus, it is necessary to develop new TADF macrocycles. In our previous work, our group developed a simple and general strategy for the synthesis of functional biphen[*n*]arenes where functional groups can be conveniently introduced into their backbone through a pre-modification and post-cyclization method.[12] In general, V-shaped precursors produce biphen[2]arenes as the only cyclic products in high yields. Theoretically, biphen[3]arenes should be formed by alternately connecting three precursors up and down, and the whole molecule has no obvious strain. In terms of the macrocyclic synthesis reaction, Friedel–Crafts (FC) alkylation is reversible and recorrecting.[13] Accordingly, we believe that biphen[3]arenes based on V-shaped units may be able to be synthesized and we predict that they would emit stronger emission than the precursor.

In this work, *N*-substituted carbazoles have been selected as the V-shaped units and pristine TADF building blocks. Four trimeric macrocycles have been successfully synthesized. When $BF_3{\cdot}Et_2O$ is used as a catalyst, it tends to form a dimer. When the catalyst is replaced with trifluoroacetic acid, trimers and dimers can be yielded simultaneously. Experimental results and theoretical calculations indicate that all macrocycles have a narrow energy gap ($\Delta E_{ST} < 0.3$ eV), which signifies their TADF emission. Importantly, all trimeric macrocycles exhibit higher quantum yields than the corresponding monomers, especially the 2,4,6-triphenyl-*s*-triazin-based macrocycle, whose quantum yield greatly increased from 36.8% to 70.9%.

The synthesis of TADF macrocycles is shown in Fig. 1. Carbazole as a donor and blocks (2,4,6-triphenyl-*s*-triazin,

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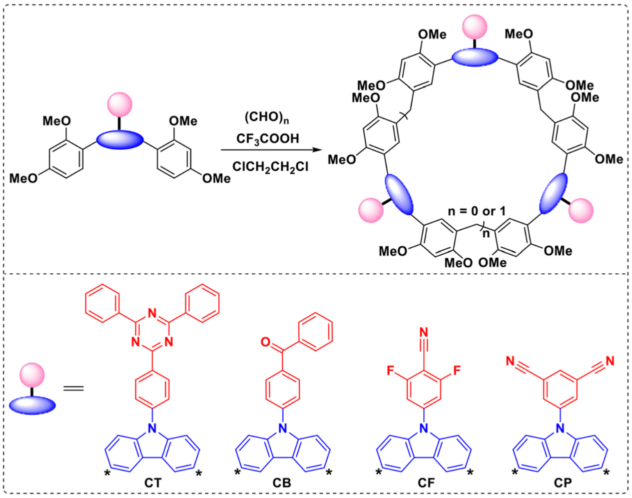

Fig. 1 The synthetic route of the target macrocycles.

benzophenone, 2,6-difluorobenzonitrile and isophthalonitrile) as acceptors were used to construct strong donor–acceptor (D–A) architectures, which can reduce the energy gap (ΔE_{ST}) between the lowest-lying singlet (S_1) and triplet (T_1) states.[14] The 2,4-dimethoxyphenyl group connecting the 3,6 positions of carbazole can enhance the electron donating ability of the donor and provide a reactive site for macrocyclic arenes. To explore the reaction conditions of the trimers, the V-shaped monomer based on CT was chosen as a model. Subsequently, we tried a cyclization reaction of this model and paraformaldehyde in the presence of 1.0 equivalent $BF_3{\cdot}Et_2O$. The reaction proceeded smoothly, but only the dimer was successfully produced after many attempts. When excessive trifluoroacetic acid was used as a catalyst, the reaction was completed within two hours and succeeded in producing the cyclic trimer (CT-3, isolated yield 5.4%). It is worth noting that if the amount of trifluoroacetic acid is below 10 equivalents, the reaction time will exceed 24 hours. Under similar conditions, other trimer macrocycles (CB-3, CF-3, and CP-3) were also obtained, and their yields reached 10.6%, 16.2% and 13.3%, respectively. We failed to obtain the ^{13}C NMR spectrum for CF-2 due to its poor solubility in organic solvents. All other compounds were characterized by ^{1}H and ^{13}C NMR spectroscopy and high resolution mass spectroscopy (HRMS, Fig. S1–S35, ESI†).

To understand the structure of these trimers, several attempts at crystallization have been made but we did not succeed in obtaining suitable single crystals for XRD analysis. The configurations of CT-3, CB-3, CF-3 and CP-3 were optimized on the basis of density functional theory (DFT) calculations at the B3LYP/6-31G(d) level of theory. As shown in Fig. 2a, these simulated structures have a triangular-prism structure where the six 2,4-dimethoxyphenyl groups of the three V-shaped precursors are alternatively linked by three methylene groups.

To confirm the TADF emission of these macrocycles, time-dependent DFT (TD-DFT) calculations were performed. The frontier molecular orbitals and energy levels of the target macrocycles in excited states were determined at the PBE0/6-31G(d) level of theory. As depicted in Fig. 2b, the HOMOs are mainly delocalized on the carbazolyl and 2,4-dimethoxyphenyl groups, while their LUMOs are distributed throughout the acceptors. The separations of the frontier orbitals suggest the charge transfer properties of these macrocycles. The calculated ΔE_{ST} values are 0.203 eV, 0.092 eV, 0.224 eV and 0.097 eV for CT3, CB3, CF3 and CP3, respectively. The small ΔE_{ST} values indicate the RISC from T_1 to S_1 and consequently efficient TADF emission.

To further investigate the TADF properties of these macrocycles, their photophysical properties were investigated. The absorption spectra of the monomers and macrocycles in toluene solution were firstly measured. They all exhibit two absorption bands in the range of 282–297 nm and 336–394 nm (Fig. S36, ESI†). The former is mainly attributed to the π–π* transition, while the latter can be assigned to the intramolecular CT transition. Photoluminescence (PL) spectra of the macrocycles in various diluted solutions were measured. As shown in Fig. S37 (ESI†), apparent solvatochromism phenomena were observed for the trimers, which suggests their strong intramolecular charge transfer (ICT) characteristics. The fluorescence (Fl) spectra at 300 K and phosphorescence (Ph) spectra at 77 K of four macrocycles in toluene solution were recorded. The onset of Fl and Ph was used to determine the experimental S_1 and T_1 values (Fig. 3 top). Then, the ΔE_{ST} values were calculated to be 0.104 eV, 0.237 eV, 0.228 eV and 0.071 eV for CT-3, CB-3, CF-3 and CP-3, respectively, which are small enough to prompt efficient reverse intersystem crossing. Moreover, the PL intensity of the macrocycles in dilute toluene is obviously enhanced after N^2 purging (Fig. 3 bottom). The sensitivity of PL intensity to oxygen coincides with the TADF luminescence mechanism. The transient PL decay curve revealed their microsecond-scale fluorescence lifetimes (Fig. S38, ESI†), further confirming their TADF emission. For comparison, the optical properties of the monomers and biphen[2]arenes are shown in Fig. S39–S47 (ESI†) and summarized in Table 1. Finally, the absolute photoluminescence quantum yields (PLQYs) in dilute toluene solution were determined. The PLQY values of four trimer macrocycles were determined to be 70.9%, 36.4%, 42.4% and 16.1% for CT-3, CB-3, CF-3 and CP-3, respectively. By contrast, the PLQY values of the corresponding monomers decreased to 36.8%, 14.7%, 42.2% and 10.8%. The results indicate that these trimers show a macrocyclization-enabled TADF. The improvement in TADF efficiency is mainly attributed to macrocyclization-induced rigidity.[15] As shown in Table S1 (ESI†), CT-3 and CB-3 exhibit larger radiative decay rate constants and smaller non-radiative decay rate constants than the corresponding monomers which helps the macrocycles to have a higher quantum yield. CF-3 has radiative and non-radiative decay rate constants similar to CF-1. Thus, CF-3 displays a negligible luminescence enhancement. CP-3 has a greater radiative decay rate constant than CP-1 and a similar non-radiative decay rate constant. Moreover, all trimers have larger RISC rates than the monomers, which is more conducive to triplet exciton utilization. Finally, control

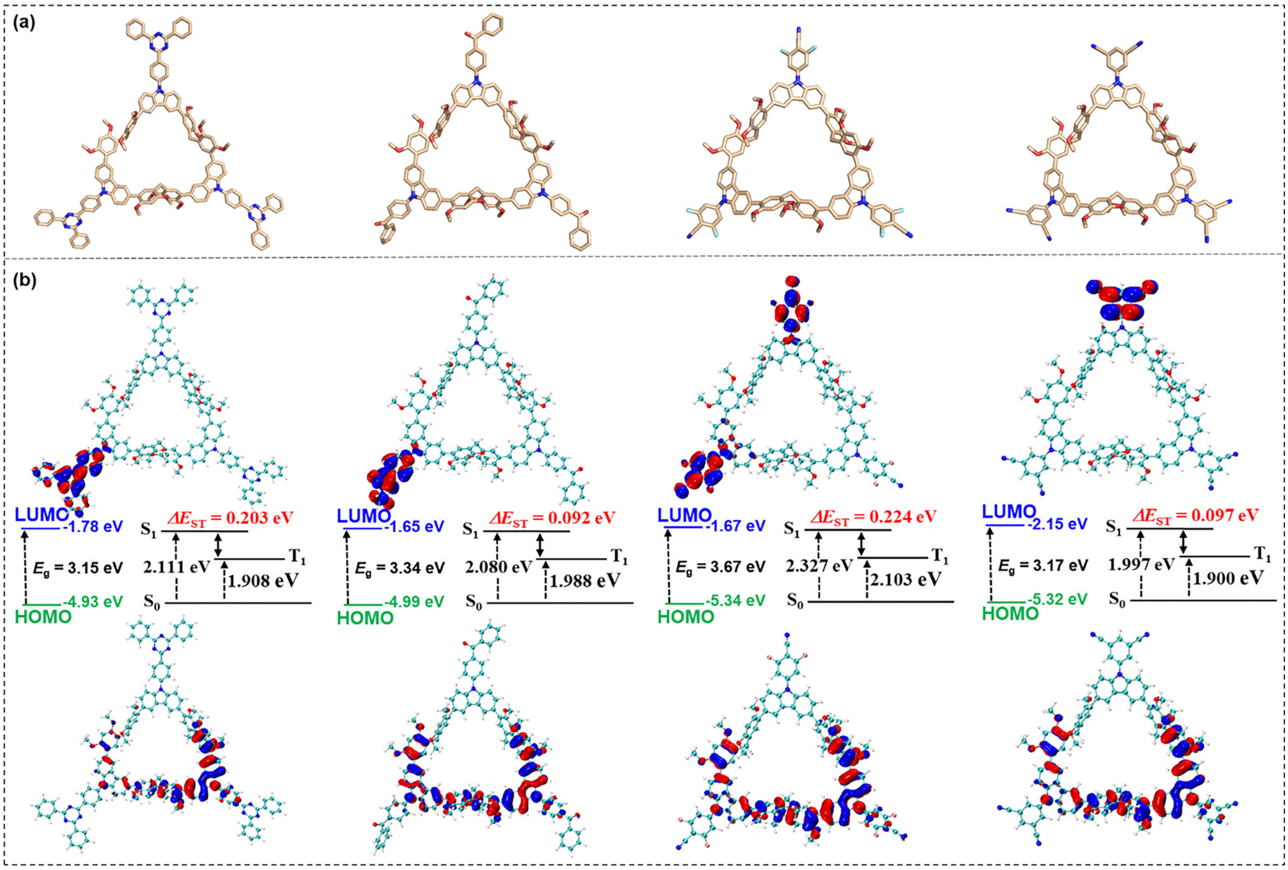

Fig. 2 (a) The energy-minimized conformation of the trimer macrocycles; (b) the optimized ground state geometries, orbital distributions, and energy levels of the lowest-lying excited singlet and triplet states of the trimer macrocycles.

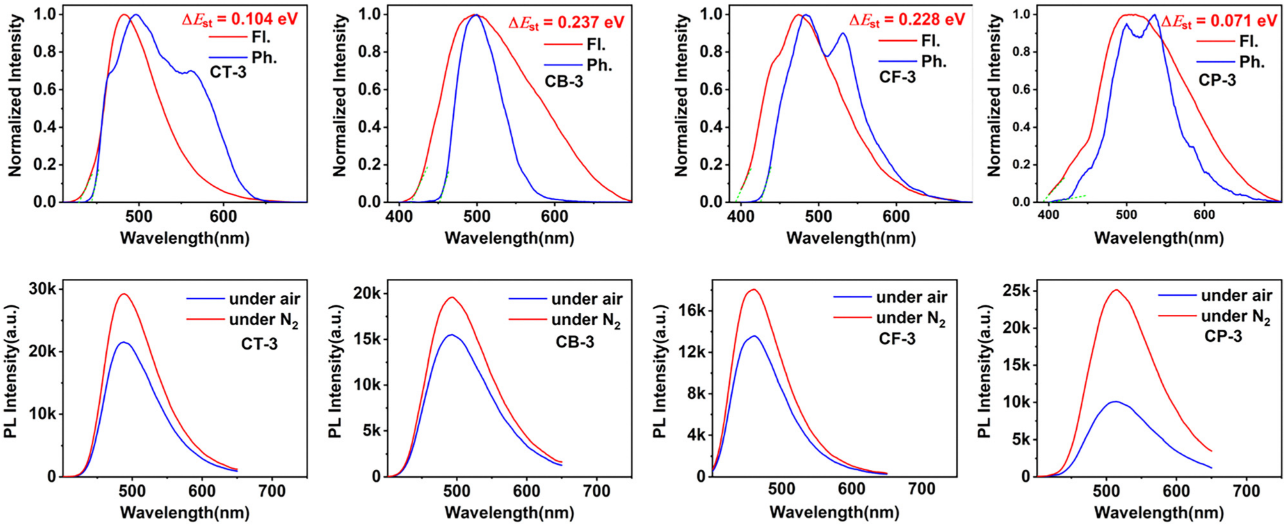

Fig. 3 Normalized fluorescence at 300 K and phosphorescence spectra at 77 K recorded in toluene (1.0×10^{-5} mol L^{-1}) of trimeric macrocycles (top); PL spectra of trimeric macrocycles in toluene (1.0×10^{-5} mol L^{-1}) before and after nitrogen purging (bottom).

experiments on the donor–acceptor monomer units were performed. As depicted in Fig. S48 (ESI†), enhanced photoluminescence was observed in the PL spectra. Although the magnitude of improvement has decreased, the quantum yield (Φ_{PL}) of the trimers is still higher than that of the corresponding monomer (Table S2, ESI†).

Table 1 Photophysical data of the monomers and macrocycles

Compound	Emission (nm)	Lifetime (μs)	PLQY (%)	ΔE_{ST} (eV)
CT-1	470	5.31	36.8	0.147
CT-2	480	4.85	34.3	0.196
CT-3	488	5.30	70.9	0.104
CB-1	476	4.08	14.7	0.198
CB-2	487	4.37	38.7	0.240
CB-3	492	4.29	36.4	0.237
CF-1	447	4.39	42.2	0.173
CF-2	454	4.32	73.4	0.127
CF-3	460	4.33	42.4	0.228
CP-1	505	4.65	10.8	0.259
CP-2	516	4.38	11.1	0.119
CP-3	514	4.50	16.1	0.071

In conclusion, a class of biphen[*n*]arene-based TADF macrocycles has been conveniently synthesized by the Friedel–Crafts alkylation reaction. Such biphen[3]arenes based on V-shaped units were reported for the first time. Importantly, trimeric macrocycles with four different luminophores show significantly higher TADF efficiency compared to the corresponding monomers. This research provides a new platform to construct novel and efficient luminescent materials.

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Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the ESI.†

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