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Aryl carbazole-based macrocycles: synthesis, their remarkably stable radical cations and host-guest complexation with fullerenes†

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A series of fully conjugated macrocycles $\mathbf{M_n}$ (n=4-7) consisting of N-(3,5-di-tert-butyl-4-methoxyphenyl) substituted carbazole (\mathbf{Cz} - \mathbf{Ar}) were successfully synthesized. The aryl carbazole and macrocycle $\mathbf{M_4}$ can be readily oxidized and the corresponding radical cation species were found to be highly stable. Moreover, macrocycle $\mathbf{M_5}$ was found to form 1:1 stoichiometric complexes with fullerenes C_{60} and C_{70} with association constants as high as (8.38 ± 0.33) \times 10^4 M^{-1} and (7.64 ± 0.26) \times 10^4 M^{-1} , respectively.

Carbazole is one of the most commonly used building blocks for a wide range of organic electronic applications such as organic solar cells (OSCs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs) and so on.¹ The inherent electron-donating ability of carbazole facilitates its hole-injection and transport, which are very conducive to realizing the excellent optoelectronic properties of carbazolebased organic functional materials, such as their good conductivity and high photoluminescence efficiency.2 Generally, the hole-injection process of the carbazole-based materials is often accompanied by the formation of a carbazole radical cation species (sometimes called a polaron), which has been intensively investigated in the fields of OSCs and OLEDs. However, the precise structural characterization of the carbazole radical cation species is relatively rare, especially the lack of the X-ray diffraction structure.3 This is largely due to the fact that most carbazole radical cation species are highly reactive and readily undergo dimerization and polymerization, and therefore usually unstable.4

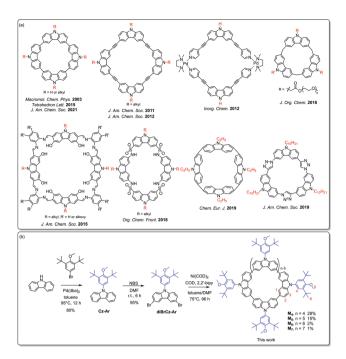
Supramolecular macrocycles containing a variety of building blocks such as phenol,⁵ pyrrole,⁶ glycoluril,⁷ para-dialkoxybenzene⁸ and so on⁹ are well known as guest receptors in supramolecular host–guest chemistry. Carbazole, one of the most common building blocks in organic synthesis,^{1,2} has also been widely used as a versatile building unit in supramolecular chemistry. Carbazole has several distinct merits such as its facile synthesis and easy modification, its structural rigidity

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with a well-defined molecular geometry, and its intriguing redox-active and luminescence properties, which make it ideal for the synthesis of a number of shape-persistent macrocycles with unique structures, novel properties, and potential applications. During the past decades, a variety of carbazole-based macrocyclic systems, including tricarbazole triazolophanes, 10 carbazole-based Schiff base macrocycles, 11 carbazolophanes, 12 calix[n]carbazole, 13 conjugated polycarbazoles, 14 cyclo[4]carbazole, 15 carbazole-ethynylene macrocycles, 16 azacalix[2]arene[2] carbazoles, 17 carbazole-based metallacycles 18 and so on, 19 have been successfully developed, and some of them have been shown to have potential applications in molecular recosupramolecular gnition, catalysis, and self-assembly (Scheme 1a). Notably, the nitrogen atom of the carbazole unit in most of the documented carbazole-based macrocycles is substituted with the alkyl side-chain, while aryl carbazole based macrocycles still remain unexplored. We infer that the substitution of the aryl group on the nitrogen atom of carbazole would have a pronounced effect on the properties of the resultant aryl carbazole based macrocycles.

In this work, we have designed and synthesized a series of fully conjugated macrocycles \mathbf{M}_n (n=4–7) consisting of N-(3,5-di-tert-butyl-4-methoxyphenyl) substituted carbazole (Cz-Ar) (Scheme 1b). The introduction of the 3,5-di-tert-butyl-4-methoxyphenyl group at the nitrogen atom of the carbazole reduced the ionization energy and enhanced the stability of the carbazole radical cation. Consequently, a mixed-valence radical cation of (\mathbf{diBrCz} - \mathbf{Ar})₂^{*+} was successfully isolated in a stable single crystal form for the first time. The stability of the carbazole radical cation was further enhanced within the framework of \mathbf{M}_4 because of the efficient spin delocalization through the enlarged macrocyclic π -system. Moreover, the interesting host-guest interactions between these aryl carbazole-based macrocycles and fullerenes were also investigated.



Scheme 1 (a) Chemical structures of some representative carbazolebased macrocycles in the literature. (b) Synthesis of the macrocycles M_n (n = 4-7) consisting of N-(3,5-di-tert-butyl-4-methoxyphenyl) substituted carbazole (Cz-Ar).

Results and discussion

As shown in Scheme 1b, N-(3,5-di-tert-butyl-4-methoxyphenyl) substituted carbazole (Cz-Ar) was prepared through the Buchwald-Hartwig amination of carbazole with 5-bromo-1,3di-tert-butyl-2-methoxybenzene in 80% yield. Bromination of Cz-Ar using N-bromosuccinimide in a dichloromethane (DCM) solution gave N-aryl-3,6-dibromocarbazole (diBrCz-Ar) in 95% yield. Subsequently, the Ni(cod)2/bpy-mediated homocoupling of diBrCz-Ar afforded a series of macrocycles M_n (n = 4-7), ¹⁵ which were successfully separated and purified by preparative gel permeation chromatography (GPC), using DCM as an eluent. The tetramer M₄, pentamer M₅, hexamer M₆ and heptamer M₇ were obtained in 28%, 15%, 2% and 1% yields, respectively, and they exhibited excellent solubility in common organic solvents. The modest yields of M₄ and M₅ were attributed to the bulky aryl substituent which significantly enhanced their solubilities. In contrast, the Yamamoto homocoupling of N-butyl-3,6-dibromocarbazole (diBrCz-C4) gave the main product of the tetramer C4-M4, while other bigger analogues including the pentamer were hardly isolated due to their extremely low yields, which are mostly caused by their low solubilities (Fig. S1†).15 The structures of Cz-Ar, diBrCz-Ar, and macrocycles \mathbf{M}_n were thoroughly characterized by ¹H and ¹³C NMR and HR-MS measurements (see the ESI†).

Single crystals suitable for X-ray crystallographic analysis were obtained for M4 and M5 by slow diffusion of methanol into chloroform solution (Fig. 1), which unambiguously confirmed their macrocyclic structures. Tetramer M4 adopted a

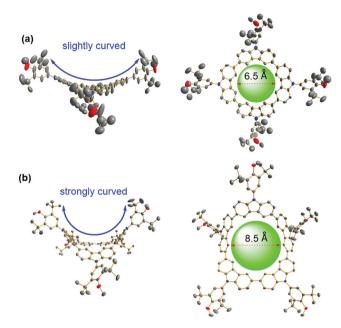


Fig. 1 Crystal structures of tetramer M_4 (a) and pentamer M_5 (b). Ellipsoids are represented with 50% probability. Hydrogen atoms and the solvent are omitted for clarity.

slightly curved conformation in the crystalline state (Fig. 1a), in contrast to the nearly planar structure of its N-alkyl substituted analogue C4-M4. 15c Macrocycle M5 further twisted and adopted a saddle-shaped conformation (Fig. 1b). The cavity diameters of M_4 and M_5 were determined to be approximately 6.5 and 8.5 Å, respectively. The curved conformations and defined cavities of M₄ and M₅ may make them ideal host candidates to recognize fullerenes (vide infra). All attempts to grow single crystals for hexamer M_6 and heptamer M_7 were unsuccessful. Therefore, a computational prediction of their conformations was performed at the RB3LYP/6-311G(d,p) level of theory. The calculated molecular geometries of hexamer M6 and heptamer M7 revealed that the macrocycles became further distorted with the increase of their size (Fig. S8 and S9†).

To evaluate the effect of N-alkyl and N-aryl substituents on the ionization potential of carbazole, the redox properties of diBrCz-Ar and diBrCz-C4 were investigated by cyclic voltammetry (CV) in CH_2Cl_2 solution (potentials are referred vs. Fc/Fc^+) (Fig. S2†). The CV of diBrCz-Ar and diBrCz-C4 exhibited one reversible oxidation wave with half-wave potentials of $E_{1/2}$ = +0.94 V and +1.10 V, respectively. The ionization potential (IP) of diBrCz-Ar was estimated to be 5.26 eV, which was lower than that of diBrCz-C4 (IP = 5.35 eV), indicating that the aryl substituent group could really reduce the ionization potential of carbazole (Table S1†). Interestingly, the CV of tetramer M4 showed four quasi-reversible oxidation waves (Fig. S3†), and its ionization potential (IP = 4.66 eV) was significantly decreased compared with that of diBrCz-Ar (Table S1†). The reversible voltammogram means that the radical states of diBrCz-Ar and tetramer M4 are most likely to be very stable, which directs us to investigate their radical cation species.

Research Article

The synthesis of the stable carbazole radical cation is highly difficult arising from the relatively high oxidation potential of carbazole and the high reactivity/instability of the carbazole radical cation.^{3,4} For example, unlike triarylamine derivatives that can be readily oxidized by some common oxidants such as AgSbF₆, SbCl₅, Cu(ClO₄)₂ and so on, N-substituted carbazole compounds encounter the difficulty of effective one-electron oxidation under mild reaction conditions. Besides, most of the N-substituted carbazole compounds undergo the dimerization or polymerization reaction during the oxidation process, resulting in major difficulties in the isolation and precise structural characterization of the carbazole radical cation species.⁴ As a consequence, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDO) was employed as an oxidant because of its strong electron-withdrawing ability. The solution of diBrCz-Ar immediately turned green after the addition of DDQ (Fig. 2a), implying the successful generation of the corresponding radical cation species (diBrCz-Ar*+).4b More specifically, the resultant green solution showed near-IR absorption beyond 1000 nm and this might suggest the formation of a singly charged primer, which was also observed in charged carbazole derivatives 20 and other π -systems. 21 The electron paramagnetic resonance (EPR) spectrum of diBrCz-Ar⁺ provided direct evidence for the presence of the radical species (Fig. 2b, blue solid line). In comparison, tetramer M₄ could be oxidized by DDQ as well as AgSbF6 due to its lower ionization potential (Fig. 2a), which is consistent with the voltammogram results. The EPR spectrum of M4*+ exhibited a strong single line in CH₂Cl₂ at room temperature (Fig. 2a, red solid line), implying efficient spin delocalization throughout the conjugated macrocycle. Notably, the radical cation species of diBrCz-Ar $^{+}$ and M_4 $^{+}$ were extremely stable, as evidenced by their almost unchanged UV-vis absorption spectra for up to one week (Fig. 2c, S4 and S5†). In contrast, the N-alkyl substituted analogue diBrCz-C4 could only be oxidized by DDQ in the presence of a strong acid (e.g., methanesulfonic acid). 4b Moreover, the resultant radical cation species was very reactive, making it nearly impossible to purify and isolate diBrCz-C4*+.

The calculation results indicated that the spin density of the

carbazole radical can be delocalized on the aryl group as well as the whole macrocycle, which might account for the enhanced stability of the radical cation species of diBrCz-Ar*+ and M4*+ (Fig. S10 and S11†).

Fortunately, single crystals of the carbazole radical cation species suitable for X-ray crystallographic analysis were successfully obtained by slow evaporation of the dichloromethane solution (Fig. 3). Interestingly, crystal structure analysis revealed a chemical moiety with a formula of (diBrCz-Ar)2(DDQ). Two diBrCz-Ar molecules were associated into inversion-centred dyads, which further alternated with one DDO molecule into a one-dimensional (1D) chain along the b-axis, wherein face-to-face packing was observed in the dimerized diBrCz-Ar (Fig. 3a). In contrast, the packing motif of the neutral diBrCz-Ar was different from those of (diBrCz-Ar)2(DDQ) and two diBrCz-Ar molecules stacked in an offset fashion (Fig. 3b). The large bond length alternation found in the aromatic ring of DDQ suggested a mixed-valence state in (diBrCz-Ar)2.+(DDQ)- rather than a full charge-transfer in $(diBrCz-Ar)_2^{2^{*+}}(DDQ)^{2^{-}}$ (Fig. S24†). Thus, the carbazole radical cation species generated herein could be regarded as a mixed-valence radical cation of (diBrCz-Ar)2.+. To the best of

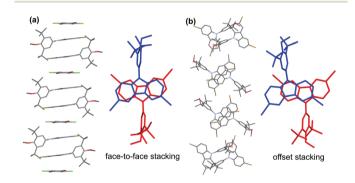


Fig. 3 The crystal structures and packing motifs of (diBrCz-Ar)₂(DDQ) (a) and diBrCz-Ar (b). Hydrogen atoms and the solvent are omitted for

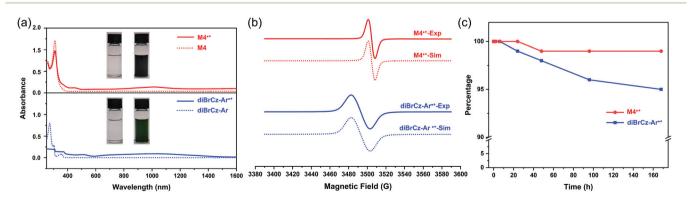


Fig. 2 (a) UV-vis-NIR spectra of diBrCz-Ar (blue line, bottom) and M4 (red line, top) before (dashed line) and after (solid line) oxidation. The insets show the photographs of the solutions of neutral and oxidized diBrCz-Ar (bottom) and M₄ (top). (b) EPR spectra and simulations of diBrCz-Ar⁻⁺ (blue line, bottom) and M_4^{-+} (red line, top). (c) Evaluation of the stability of the radical cation species of diBrCz-Ar⁻⁺ (blue column) and M_4^{-+} (red column) using UV-vis-NIR spectroscopy.

our knowledge, this is the first time that a quality crystal of the carbazole radical cation was presented.3 All attempts to grow single crystals for radical cation $\mathbf{M_4}^{\star +}$ were unsuccessful. Thus, the structure of $\mathbf{M_4}^{*+}$ was simulated at the UB3LYP/6-311G(d,p) level of theory (Fig. S11b†), wherein the spin density was fully delocalized over the whole molecule (Fig. S11c†).

Since tetramer M_4 and pentamer M_5 were relatively electron rich and possessed the distinct curved conformations and defined cavities, we speculated that they may serve as macrocyclic receptors towards fullerene recognition. The host-guest interactions between the macrocycles and fullerenes C60 and C₇₀ were first examined by NMR spectroscopy. The ¹H NMR spectrum of M4 remained unchanged when mixed with fullerene C₆₀ or C₇₀, implying negligible host-guest interactions between M4 and the fullerenes (Fig. 4a). Indeed, the cavity diameter (\sim 6.5 Å) of M_4 did not match well with the size of the fullerenes (~7.1 Å), and thus, it was too small to associate with them. In contrast, the addition of C₆₀ or C₇₀ to a solution of pentamer M_5 in toluene- d_8 resulted in an obvious downfield shift of proton H¹ and slight upfield shifts of protons H², H³,

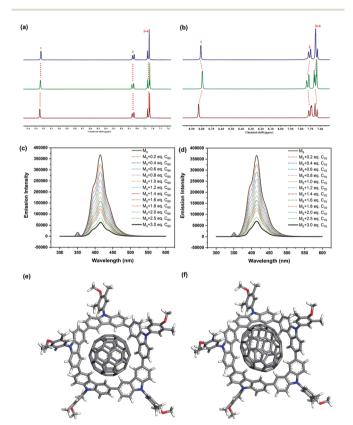


Fig. 4 (a) Partial ¹H NMR spectra (400 MHz, toluene-d₈, 298 K) of solutions of 2.0 mM M_4 + 2.0 mM C_{70} (top), 2.0 mM M_4 (middle), and 2.0 mM M_4 + 2.0 mM C_{60} (bottom). (b) Partial ¹H NMR spectra (400 MHz, toluene- d_8 , 298 K) of solutions of 2.0 mM M_5 + 2.0 mM C_{70} (top), 2.0 mM M_5 (middle), and 2.0 mM M_5 + 2.0 mM C_{60} (bottom). (c) Complexation process of M_5 and C_{60} . (d) Complexation process of M_5 and C_{70} . (e) Top view of the optimized geometry of $M_5 \supset C_{60}$ at the RB3LYP-D3/6-311+G(d,p) level of theory. (f) Top view of the optimized geometry of $M_5 \supset C_{70}$ at the RB3LYP-D3/6-311+G(d,p) level of theory.

and H4 of M5 (Fig. 4b), illustrating their considerable hostguest interactions. The observed set of NMR peaks suggested that the host-guest complexation between M5 and the fullerenes was a fast-exchange process within the NMR timescale at 298 K.⁹¹ Moreover, the significant downfield shift of the inner proton H¹ was likely to indicate that the fullerenes might be encapsulated within the curved surface of M_5 . In addition, the fluorescence intensity of M_5 was quenched constantly with increasing concentration of C₆₀ and C₇₀ (Fig. 4c and d), further indicating their distinct host-guest interactions. To determine the binding stoichiometry of M₅ and the fullerenes, the titration data were firstly obtained using the nonlinear regression models. The data were fitted to the association equilibria corresponding to the formation of inclusion complexes of 1:1 and 2:1 stoichiometries and a mixture of the two, respectively. Only the 1:1 model met the data, which indicated the presence of a 1:1 complex. Subsequently, Job plot analysis and MALDI-TOF MS also revealed a 1:1 stoichiometry of the complexation of M_5 and the fullerenes (Fig. S18 and S19†). Fluorescence titration experiments in toluene solution also provided the association constants of $(8.38 \pm 0.33) \times 10^4 \text{ M}^{-1}$ and $(7.64 \pm 0.26) \times 10^4 \text{ M}^{-1}$ for $\mathbf{M}_5 \supset C_{60}$ and $\mathbf{M}_5 \supset C_{70}$, respectively, by fitting the concentration-dependent change of the emission intensity of M5. The moderate association constants unambiguously demonstrated the existence of the hostguest interactions between M_5 and the fullerenes. Furthermore, the additional peak observed in the UV-vis spectrum of the mixture of M₅ and C₆₀ revealed the intriguing charge transfer interactions between the electron-rich M5 and the electron-deficient fullerene (Fig. S17†). To gain insight into the structural information of the host-guest complex and their host-guest interaction, molecular mechanics simulations at the RB3LYP-D3/6-311+G(d,p) level of theory were also performed. The simulated structures of the host-guest complexes $\mathbf{M}_5 \supset C_{60}$ and $\mathbf{M}_5 \supset C_{70}$ revealed that the fullerenes fitted perfectly inside the concave cavity of M_5 through multiple π - π interactions (Fig. 4e and f). Therefore, the above results indicate that both the electron-rich nature of M5 and its distinct curved conformation play a key role in fullerene recognition.

Conclusions

In summary, we have successfully synthesized a series of fully conjugated aryl carbazole-based macrocycles \mathbf{M}_n (n = 4-7) bearing a 3,5-di-tert-butyl-4-methoxyphenyl substituent. The bulky aryl group not only improved the solubility of the macrocycles but also reduced the ionization potential of the carbazole building block as well as the macrocycles. As a consequence, the aryl carbazole and M_4 were readily oxidized into radical cation species in the presence of DDQ. The resultant radical cation species were found to be very stable because the spin density can be delocalized on the aryl group as well as the whole macrocycle. Notably, a mixed-valence radical cation of (diBrCz-Ar)2* was successfully isolated and confirmed by X-ray crystallography. Moreover, pentamer M5 possessed a curved

conformation and defined cavity, making it an ideal macrocyclic host candidate to recognize fullerenes. The excellent fullerene recognition ability of \mathbf{M}_5 was also attributed to the electron-rich nature of aryl carbazole, leading to the obvious charge transfer interactions between \mathbf{M}_5 and \mathbf{C}_{60} . The arylfunctionalization strategy in this study will shed some light on the design of novel macrocyclic arenes, which may exhibit some distinct properties compared with their alkyl substituted analogues.

Conflicts of interest

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There are no conflicts to declare.

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