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Synthesis and Photophysical Properties of Doubly β-to-β Bridged Cyclic Zn^{II} Porphyrin Arrays

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Abstract: A series of doubly β-to-β bridged cyclic Zn^{II} porphyrin arrays were prepared by a stepwise Suzuki–Miyaura coupling reaction of borylated Zn^{II} porphyrin with different bridge groups. The coupling of the building block of β,β′-diboryl Zn^{II} porphyrin **1** with different bridges provided the doubly β-to-β carbazole-bridged Zn^{II} porphyrin array **3**, the fluorene-bridged Zn^{II} porphyrin array **5**, the fluorenone-bridged Zn^{II} porphyrin array **7**, and the three-carbazole-bridged Zn^{II} porphyrin ring **8**. The structural assignment of **3** was confirmed by the X-ray diffraction analysis, which revealed a highly symmetrical and remarkably bent syn-form structure. The incorporation of bridge units with different electronic effects results in different photophysical properties of the cyclic Zn^{II} porphyrin arrays. Comprehensive photophysical studies demonstrate that the electron-withdrawing bridge fluorenone has the largest electronic interaction with the Zn^{II} porphyrin unit among the series, thus resulting in the highest two-photon absorption cross-section values ($\sigma^{(2)}$) of 6570±60 GM for **7**. The present work provides a new strategy for developing porphyrin-based optical materials.

Keywords: conjugation · cross-coupling · macrocycles · porphyrinoids · two-photon absorption

Introduction

Porphyrin, as a versatile molecule, plays an important role in both natural photosynthetic systems and in the chemistry world. The wide use of porphyrin-based chromophores in fields such as host–guest chemistry, material chemistry, and molecular photochemistry, has evoked extensive interest in the synthesis and functionalization of porphyrinic molecules. Recently, covalently linked porphyrin oligomers have drawn much attention because of their potential applications in molecular electronic devices,[1] dye-sensitized solar cells (DSSCs),[2] and nonlinear optical materials.[3] Among these oligomers, cyclic porphyrin arrays constructed by means of covalent bonds are particular attractive because of their unique electronic properties that differ from their linear analogues.

Progress in the synthesis of porphyrin arrays relies on the development of new coupling reactions. The synthesis of *meso*-to-*meso* linked Zn^{II} porphyrin arrays by $AgPF_6$-promoted oxidation of 5,15-diaryl substituted Zn^{II} porphyrin launched a new area of synthetic porphyrin chemistry, yielding large linear, cyclic, and sheet Zn^{II} porphyrin arrays.[4] Up to now, most covalently bonded cyclic porphyrin arrays reported were constructed by using the *meso*-to-*meso* bridging method,[5] and only a few studies have dealt with the synthesis of β-to-β bridged cyclic porphyrin arrays. As another effective synthetic protocol, the introduction of suitable groups at β-positions also has a significant effect on the electronic properties of porphyrins.[6] Recently, Osuka and Shinokubo et al. developed an iridium-catalyzed method for the direct borylation of porphyrin at the β-position with high regioselectivity,[7] which makes it possible to add further functionalization at this position.[6b,8] By using the building block of β-borylated porphyrin, the authors reported the synthesis of the β-to-β bridged cyclic porphyrin arrays with 1,3-butadiyne,[9] 2,6-pyridylene,[10] and 2,5-thienylene bridges,[11] and all the arrays exhibit unique photophysical properties. The double-bridging strategy endows the porphyrin arrays with stiff conformations, which allows effective π-delocalization and thus the formation of large conjugated networks. The obtained results suggest that the structure of the bridges at the β-position greatly affects the photophysical properties of cyclic porphyrin arrays.

To further clarify the bridge effect in cyclic porphyrin arrays, we report herein the synthesis of a series of β-to-

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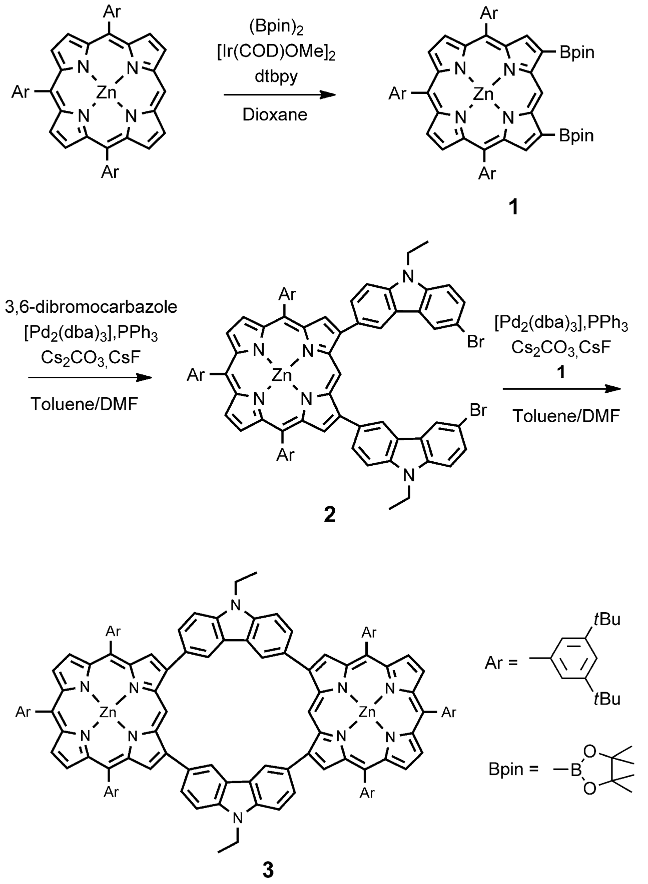
β bridged cyclic Zn^{II} porphyrin arrays with carbazole, fluorene, and fluorenone moieties as bridges. These bridges possess different electronic effects, that is, electron-donating, electroneutral, and electron-withdrawing ones for carbazole, fluorene, and fluorenone, respectively, although they have similar geometrical structures. The studies on the Zn^{II} porphyrin arrays with different bridges will disclose the relationship between the molecular structures and the photophysical properties, which will enable the design of porphyrin-based materials.

Results and Discussion

Synthesis

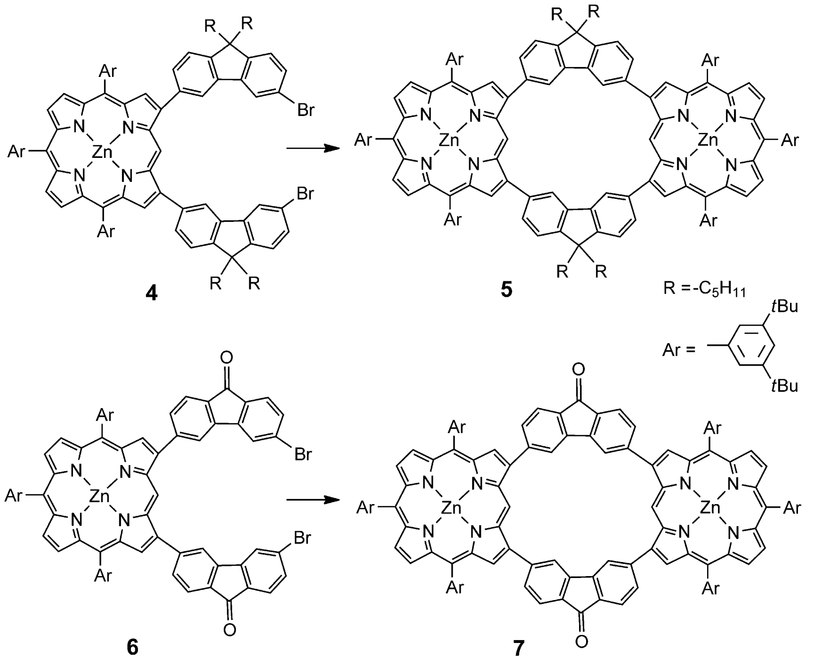
Carbazole-bridged Zn^{II} porphyrin array 3: The procedure for the synthesis of carbazole-bridged Zn^{II} porphyrin array **3** is shown in Scheme 1. Borylation of 5,10,15-*tris*(3,5-di-*tert*-butylphenyl) Zn^{II} porphyrin (1 equiv) with *bis*(pinacolato)diborane (10 equiv) in the presence of a catalytic amount of [Ir(cod)OMe]$_2$ (0.05 equiv) and 4,4′-di-*tert*-butyl-2,2′-bipyridyl (dtbpy, 0.10 equiv) in 1,4-dioxane provided a known compound of β,β′-diboryl Zn^{II} porphyrin **1**[6b] in 82 % yield. The purification of diborylated Zn^{II} porphyrin is easily accomplished by recrystallization from CH_2Cl_2/MeOH (8:1), which is more convenient than the separation of borylated free-base porphyrin by recycling preparative gel permeation chromatography–high performance liquid chromatography (GPC–HPLC).[7,12] Then the Suzuki–Miyuara coupling reaction of **1** (1 equiv) with 3,6-dibromocarbazole (5 equiv)[13] was carried out under conditions of [Pd$_2$(dba)$_3$] (0.03 equiv), PPh$_3$ (0.12 equiv), Cs_2CO_3 (2.0 equiv), and CsF (2.0 equiv) in a mixture of toluene and DMF (2:1) at 90 °C to afford β,β′-dicarbazole Zn^{II} porphyrin **2** in 76 % yield. In the same way, the double coupling of **1** with **2** furnished carbazole-bridged Zn^{II} porphyrin array **3** in 41 % yield. The lower yield of cyclization may be caused by the deborylation of **1** and the formation of linear analogues. The ^{1}H NMR spectrum of **3** in $CDCl_3$ at room temperature is simple, exhibiting one singlet at 10.33 ppm for the *meso*-protons (H_m) and two singlets at 9.00 and 8.94 ppm for the β-protons ($H_β$), thereby reflecting its highly symmetric structure. The parent ion peak of **3** was observed at *m/z* 2254.6 (calcd for $C_{152}H_{162}N_{10}Zn_2$: 2258.2 $[M]^+$) in its MALDI-TOF mass spectrum. The final structural confirmation was obtained by single-crystal X-ray diffraction analysis (see below).



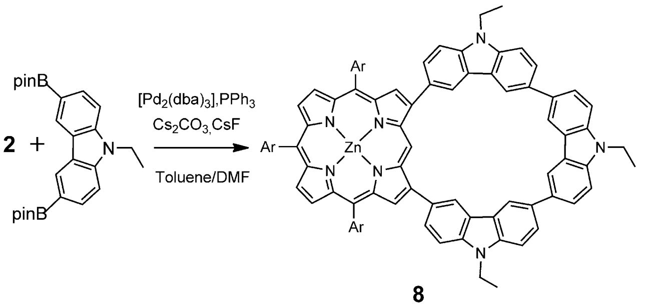
Scheme 1. Synthesis of the carbazole-bridged Zn^{II} porphyrin array **3**.

Fluorene-bridged Zn^{II} porphyrin array 5 and fluorenone-bridged Zn^{II} porphyrin array 7: The successful preparation of carbazole-bridged Zn^{II} porphyrin array **3** suggested the possibility of synthesizing cyclic Zn^{II} porphyrin arrays with other bridges. We then examined the Suzuki–Miyaura coupling of **1** with 2,6-dibromofluorene and 2,6-dibromofluorenone,[14] which have similar molecular structures but different electronegativities compared with 2,6-dibromocarbazole. With the same procedure as for the preparation of **3**, treatment of **1** with 2,6-dibromofluorene or 2,6-dibromofluorenone in the presence of [Pd$_2$(dba)$_3$] as catalyst furnished β,β′-difluorene Zn^{II} porphyrin **4** or β,β′-difluorenone Zn^{II} porphyrin **6** in yields of 80 % and 48 %, respectively. The different coupling yields may be attributed to the different electronegativities of the bridges. The double coupling reaction of **1** with **4** or **6** afforded the desired fluorene-bridged Zn^{II} porphyrin array **5** and fluorenone-bridged Zn^{II} porphyrin array **7** in 38 % and 22 % yields, respectively (Scheme 2). Both **5** and **7** exhibit simple ^{1}H NMR spectra with a singlet (H_m) at 10.27 ppm for **5** and 9.87 ppm for **7**, which are indicative of symmetrical cyclic structures. The parent ion peaks were observed at *m/z* 2477.6 for **5** (calcd for $C_{170}H_{196}N_8Zn_2$: 2480.4 $[M]^+$) and at *m/z* 2226.2 for **7** (calcd for $C_{150}H_{152}N_8O_2Zn_2$: 2228.1 $[M]^+$), respectively, in the MALDI-TOF mass spectra.

Three carbazole-bridged Zn^{II} **porphyrin ring 8:** To better understand the role of bridges in the cyclic Zn^{II} porphyrin arrays, we continued with the synthesis of the Zn^{II} porphyrin ring **8** composed of one Zn^{II} porphyrin unit and three carbazole groups. This array was obtained in 45 % yield by treatment of **2** (1 equiv) and 3,6-diborylcarbazole (1 equiv) in the presence of [Pd$_2$(dba)$_3$] as catalyst in a mixture of toluene and DMF (2:1) at 90 °C (Scheme 3). Because the synthesis of 3,6-diborylfluorene and 3,6-diborylfluorenone failed under the same conditions, we did not obtain similar struc-



Scheme 2. Synthesis of the fluorene-bridged Zn^{II} porphyrin array **5** and the fluorenone-bridged Zn^{II} porphyrin array **7**. Reagents and conditions: β,β′-diboryl Zn^{II} porphyrin **1**, [Pd$_2$(dba)$_3$], PPh$_3$, Cs$_2$CO$_3$, CsF, toluene/DMF, reflux.



Scheme 3. Synthesis of carbazole-bridged Zn^{II} porphyrin ring **8**.

tures of three fluorene- or fluorenone-bridged Zn^{II} porphyrin rings. The structure of **8** was confirmed by ^{1}H NMR spectroscopy and MALDI-TOF mass spectrometry, with a *meso* proton resonance at 10.68 ppm and a parent ion peak at *m*/*z* 1515.6 (calcd for $C_{104}H_{103}N_7Zn$: 1514.8 [M]$^+$).

X-ray Diffraction Analysis

Single crystals of the carbazole-bridged Zn^{II} porphyrin array **3** suitable for X-ray diffraction analysis were obtained by slow diffusion of methanol vapor into a toluene solution of **3**. The obtained structure is depicted in Figure 1. Clearly, the carbazole-bridged Zn^{II} porphyrin array **3** displays a remarkably bent syn-form structure with a diporphyrin dihedral angle of 93.4°, and the two carbazole bridges exhibit the same conformation with a dihedral angle of 136.2°, while the nitrogen atoms point to the outside of the cycle. The N-Zn-N angles in the Zn^{II} porphyrin unit are 165.3–167.5°, which means that the zinc atom is slightly out of the plane of porphyrin. The center-to-center distance between the zinc atoms is about 13.35 Å. The carbazole bridges are connected to the neighboring pyrroles with dihedral angles of 96.9°, 64.1°, 129.2°, and 86.5°, thus implying a limited delocalization of the porphyrin π circuits through the bridges. The bond lengths between the porphyrin and the neighboring carbazole (1.47–1.49 Å) are close to those of normal C−C single bonds (1.54 Å), further suggesting the poor conjugation between the porphyrin core and the carbazole bridge. The crystal structure validates the analysis of the ^{1}H NMR spectrum.

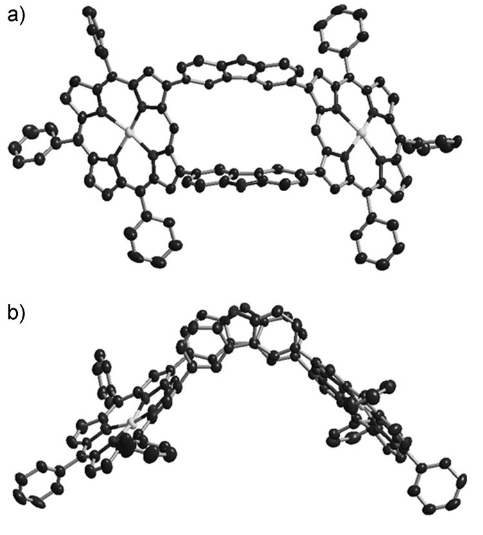


Figure 1. X-ray crystal structure of carbazole-bridged Zn^{II} porphyrin array **3**. a) Top view and b) side view. The thermal ellipsoids are drawn at the 50 % probability level. For clarity, *tert*-butyl groups, solvent molecules, and hydrogen atoms are omitted.

Photophysical Characterization of the Zn^{II} Porphyrin Arrays

The UV/Vis absorption and fluorescence spectra of the cyclic Zn^{II} porphyrin arrays **3**, **5**, and **7**, and of the 5,10,15-*tris*(3,5-di-*tert*-butylphenyl) Zn^{II} porphyrin monomer in CH_2Cl_2 are shown in Figure 2 and Figure 3, respectively. All the cyclic Zn^{II} porphyrin arrays exhibit the typical absorption characteristics of the Zn^{II} porphyrin monomer with

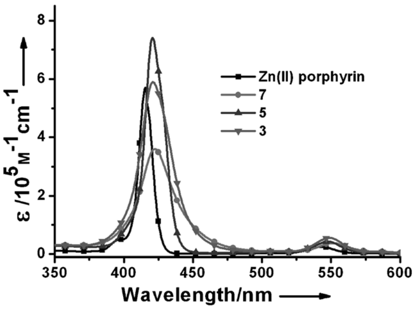


Figure 2. UV/Vis absorption spectra of the $\mathrm{Zn^{II}}$ porphyrin arrays **3**, **5**, and **7** in CH_2Cl_2.

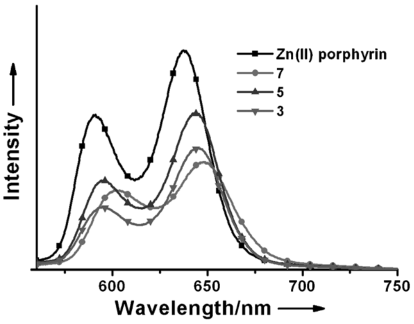


Figure 3. Emission spectra of the $\mathrm{Zn^{II}}$ porphyrin arrays **3**, **5**, and **7** in CH_2Cl_2 at $\lambda_{ex} = 550$ nm.

a strong absorption band at around 420 nm and a weak one at about 550 nm assigned to the Soret (B) band and the Q band, respectively. However, a slight bathochromic shift of the Soret band along with an obvious broadening was observed for the $\mathrm{Zn^{II}}$ porphyrin arrays compared with that of the $\mathrm{Zn^{II}}$ porphyrin monomer ($\lambda_{max} = 416$ nm). The full width at half maximum (fwhm) of the Soret bands increases in the order of **5** (930 cm^{-1}) < **3** (1469 cm^{-1}) < **7** (1651 cm^{-1}), which is indicative of increasing electronic interactions between the porphyrin segments and the bridges. The Soret and Q bands of the bridge-substituted acylic monomers **2**, **4**, and **6** exhibit a larger red shift than those of the corresponding cyclic $\mathrm{Zn^{II}}$ porphyrin arrays (Figures S21 and S22 in the Supporting Information), thus indicating that the conjugation between the bridge and the $\mathrm{Zn^{II}}$ porphyrin unit in the cyclic $\mathrm{Zn^{II}}$ porphyrin arrays is restricted by the constrained conformation. The absorption spectra of **3**, **5**, and **7** are similar to that of the previously reported β,β′-doubly 2,6-pyridylene-bridged porphyrin dimer,[10] thus suggesting a lack of intramolecular electronic interaction between porphyrin units. The fluorescence spectra of all the $\mathrm{Zn^{II}}$ porphyrin arrays exhibit typical vibronic structures with a slight bathochromic shift in comparison with the bands of the $\mathrm{Zn^{II}}$ porphyrin monomer, and the emission maxima change in the same sequence as the maxima of the Soret and Q bands. The Stokes shifts of the cyclic $\mathrm{Zn^{II}}$ porphyrin arrays are smaller than those of the corresponding acyclic ones (**2**, **4**, and **6**), further demonstrating the restriction of the geometric change of the cyclic arrays in the excited state. The Stokes shift of the cyclic array **7** is slightly larger than that of the $\mathrm{Zn^{II}}$ porphyrin monomer, thus indicating an effect of the electron-withdrawing bridge, possibly implying the formation of a sort of D-π-A structure.[15] The fluorescence quantum yields for all the $\mathrm{Zn^{II}}$ porphyrin arrays are between 0.014 and 0.025.

Fluorescence lifetimes were determined for all the molecules to obtain information about the excited states of the $\mathrm{Zn^{II}}$ porphyrin arrays. Figure S23 in the Supporting Information shows the time-resolved fluorescence decay profiles of the cyclic $\mathrm{Zn^{II}}$ porphyrin arrays, the bridge-substituted acylic monomers, and the 5,10,15-*tris*(3,5-di-*tert*-butylphenyl) $\mathrm{Zn^{II}}$ porphyrin monomer. The fluorescence lifetimes of the cyclic $\mathrm{Zn^{II}}$ porphyrin arrays and the bridge-substituted acylic monomers are similar to that of the $\mathrm{Zn^{II}}$ porphyrin monomer except the fluorenone substituted ones, which indicates a lack of the inter-porphyrin electronic communication through the bridges. The slightly shortened lifetime of the fluorenone-substituted $\mathrm{Zn^{II}}$ porphyrin compounds can be rationalized by the substituent effect and a relatively larger effect of the electron-withdrawing group, which is consistent with the results of steady-state photophysical studies. The photophysical data for the $\mathrm{Zn^{II}}$ porphyrin arrays, the bridge-substituted acylic monomers, and the $\mathrm{Zn^{II}}$ porphyrin monomer are collected in Table 1.

Table 1. Spectral properties of $\mathrm{Zn^{II}}$ porphyrin arrays and monomers in CH_2Cl_2.

	Absorption λ_{max} [nm]	Emission λ_{max} [nm]	Stokes shift [cm^{-1}]	Quantum yield	Lifetime [ns]	TPA($\sigma^{(2)}$) [GM][a]
$\mathrm{Zn^{II}}$ porphyrin	416, 543	590, 638	1467	0.033	2.2	<100
2	432, 552	608, 651	1669	0.017	2.3	760±20
3	421, 549	595, 645	1408	0.013	2.1	5330±60
4	429, 550	609, 649	1761	0.021	2.3	650±20
5	420, 547	595, 644	1475	0.019	2.1	5820±50
6	433, 552	616, 655	1882	0.005	1.8	1640±20
7	423, 552	602, 648	1505	0.014	1.8	6570±60
8	423, 549	599, 647	1520	0.025	1.9	2620±20

[a] Measured in toluene. GM, Goeppert–Mayer unit.

The two-photon absorption cross-section values ($\sigma^{(2)}$) were measured by using an open-aperture Z-scan method. An 800 nm laser was chosen as the excitation light source to completely eliminate the contribution from one-photon absorption. The open aperture Z-scan traces of the doubly β-to-β bridged $\mathrm{Zn^{II}}$ porphyrin arrays and the acylic monomers are shown in Figure 4 and Figure S24 (Supporting Information), respectively, and the obtained TPA cross-section data are given in Table 1. All the cyclic $\mathrm{Zn^{II}}$ porphyrin arrays

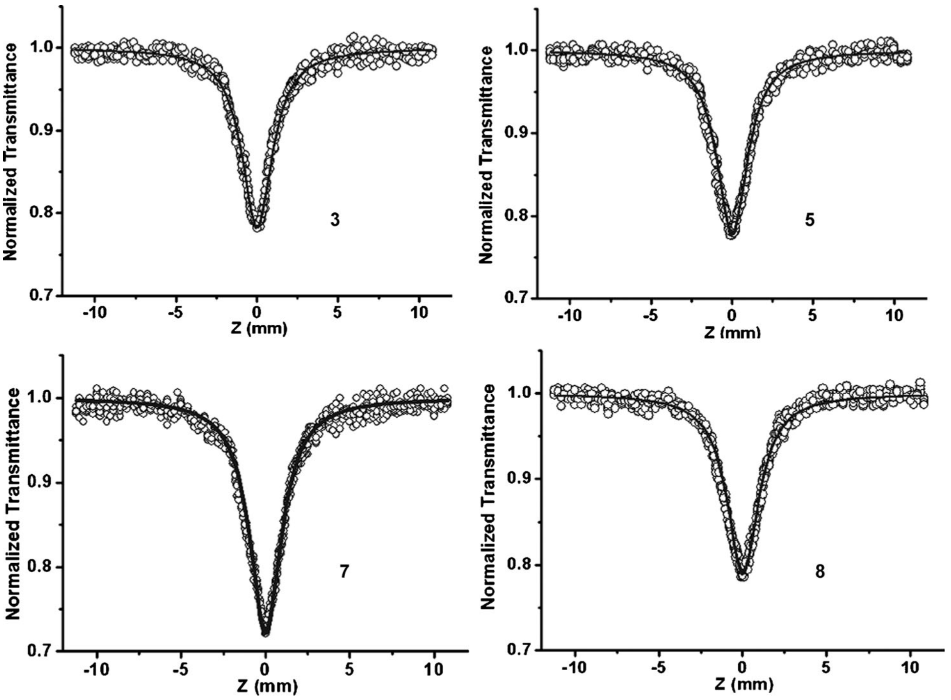


Figure 4. Open aperture Z-scan traces of doubly β-to-β bridged Zn^{II} porphyrin arrays. The solid lines are the best fitted curves of the experimental data.

show a substantial increase in the TPA cross-section values compared with the acyclic ones. Although the cyclic Zn^{II} porphyrin arrays have only one more Zn^{II} porphyrin unit than the acyclic ones, the TPA cross-section values of the cyclic arrays are six, eight, and three times higher than those of the corresponding carbazole-, fluorene-, and fluorenone-bridged acylic ones, respectively. Therefore, the increased number of the Zn^{II} porphyrin unit is not the only reason for the increase in the TPA cross-section values of the cyclic arrays. Previous reports have demonstrated that the dimensionality of conjugated molecules plays a decisive role in the TPA properties.[3c,16] This suggests that the multidimensional π delocalization and the associated molecular hyperpolarizability induced by the cyclization in the Zn^{II} porphyrin arrays also contribute significantly to the TPA cross-section. For the cyclic arrays, the TPA cross-section value increases in the order of **3**<**5**<**7**, thus indicating an effect of the bridge structures. The electron-withdrawing group has a larger effect on the enhancement of the TPA cross-section than the electron-donating and electroneutral ones, which may be attributed to the existence of a sort of D-π-A structure in **7**. To further understand the role of molecular structure, we measured the TPA cross-section value of the Zn^{II} porphyrin ring **8** under the same conditions. The TPA cross-section value of **8** (2620±20 GM) is about three times higher than that of **2** (760±20 GM). Usually, intramolecular π delocalization increases the TPA cross-section. However, the increased TPA cross-section value of **8** here cannot be ascribed to an enhanced π delocalization because the electronic interaction between the porphyrin unit and the bridge substituents in **2** is higher than that in **8** according to their absorption and emission spectra (Figure S19 and S20 in the Supporting Information). We conclude that the multidimensionality of the cyclic structure of the molecule plays the key role for the enhancement of the TPA cross-section of **8**. The TPA cross-section value of **8** is about half the value of Zn^{II} porphyrin array **3**, which further strengthens the notion of a contribution of the multidimensional cyclic structure to the TPA cross-section.

Conclusions

In summary, we have accomplished the synthesis of a series of doubly β-to-β bridged cyclic Zn^{II} porphyrin arrays by a stepwise Suzuki–Miyaura coupling reaction of borylated Zn^{II} porphyrin with carbazole, fluorene, and fluorenone as bridge structures, respectively. The single-crystal X-ray diffraction analysis of carbazole-bridged Zn^{II} porphyrin array **3** confirmed unambiguously the formation of the final cyclic structure. Based on the UV/Vis absorption and fluorescence spectra, the electronic communication between the bridge and the Zn^{II} porphyrin units is insignificant. The photophysical properties of cyclic Zn^{II} porphyrin arrays can be modulated by altering the coupling bridges, and the electron-withdrawing bridge results in more obvious effects. The present work provides a new strategy for the development of porphyrin-based optical materials.

Experimental Section

Materials

Reagents were purchased from Acros, Alfa Aesar, or Beijing Chemicals and used without further purification unless otherwise noted. 1,4-dioxane and dichloromethane (CH_2Cl_2) were dried with sodium and CaH_2, respectively, and distilled under a N_2 atmosphere. All solvents used for spectroscopic measurements were spectral grade.

Instrumentation

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained on a Bruker Avance Π-400 spectrometer with tetramethylsilane as an internal standard. MALDI-TOF-MS spectra were measured on a Bruker BIFLEX III spectrometer. Elemental analyses were carried out on a Flash EA1112 elemental analyzer (Thermo Electron). Absorption and emission spectra were obtained on a Shimadzu UV-1601PC spectrometer and a Hitachi F-4500 spectrometer, respectively. Fluorescence quantum yields were determined under excitation at 550 nm, using Zn^{II} tetraphenylporphyrin (Zn-TPP) as a standard. Fluorescence decay processes were recorded with a single photon counting technique on an Edinburgh FLS920 fluorescence lifetime system, and the equipment resolution is

~0.1 ns. X-ray crystallography data were taken on a Rigaku R-axis Rapid IP diffractometer with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å).

TPA Measurements

The TPA measurements were performed using the open-aperture Z-scan method with 180 fs pulses from an optical parametric amplifier (Coherent) operating at a 1 kHz repetition rate using a Ti:sapphire regenerative amplifier system (Coherent Legend Elite ultrafast amplifier laser system). After passing through a $f = 20$ cm lens, the laser beam was focused at the center of a 1 mm-quartz cell. As the position of the sample cell was varied along the laser-beam direction (z-axis), the transmitted laser light from the sample cell was then probed by using an OPHIR laser measurement group (NOVA II, PD300-3W-V1) as used for reference monitoring.

3,6-Dibromofluorenone and 3,6-Dibromo-9,9′-dipentylfluorene

These compounds were synthesized according to a reported procedure.[14] ^{1}H NMR (400 MHz, $CDCl_3$) for 3,6-dibromofluorenone: $\delta = 7.68$ (d, $J = 1.3$ Hz, 2H), 7.55 (d, $J = 7.8$ Hz, 2H), 7.50 ppm (dd, $J = 7.9$, 1.6 Hz, 2H); ^{1}H NMR (400 MHz, $CDCl_3$) for 3,6-dibromo-9,9′-dipentylfluorene: $\delta = 7.78$ (d, $J = 1.8$ Hz, 2H, fluorene), 7.43 (dd, $J = 8.0$, 1.8 Hz, 2H, fluorene), 7.19 (d, $J = 8.0$ Hz, 2H, fluorene), 1.96–1.85 (m, 4H), 1.13–0.93 (m, 8H), 0.71 (t, $J = 6.9$ Hz, 6H), 0.65–0.46 ppm (m, 4H).

3,6-Dibromo-9-ethylcarbazole

Carbazole (3.6 g, 0.2 mmol, 1.0 equiv) and dimethylformamide (DMF) (40 mL) were added to a three-necked flask (100 mL), and a solution of *N*-bromosuccinimide (NBS) (7.6 g, 0.4 mmol, 2.0 equiv) in DMF (20 mL) was added dropwise at 0 °C. The mixture was then stirred at ambient temperature for 2 h. Subsequently, the reaction was quenched with excess water (200 mL) to produce a white precipitate, which was filtrated and recrystallized from ethanol to afford 3,6-dibromocarbazole as a white solid (5.0 g, 72.0 %, m.p. 214–216 °C). Next, 3,6-dibromocarbazole (1.6 g, 5 mmol), bromoethane (1.5 g, 7.5 mmol), DMSO (100 mL), and NaOH solution (5 mL, 50 %) were added to a three-necked flask (250 mL), and the mixture was stirred at ambient temperature for 4 h. The reaction was quenched with water and extracted with Et_2O, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by recrystallization from ether/CH_2Cl_2 to produce a white solid (1.7 g, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.14$ (s, 2H, carbazole), 7.56 (d, $J = 6.8$ Hz, 2H, carbazole), 7.27 (d, $J = 9.5$ Hz, 2H, carbazole), 4.31 (q, $J = 7.2$ Hz, 2H), 1.40 ppm (s, 3H).

3,6-Dibory-9-ethylcarbazole

3,6-Dibromo-9-ethylcarbazole (353.0 mg, 1.0 mmol, 1.0 equiv) and [Pd($PPh_3)_2Cl_2$] (70.2 mg, 0.1 mmol, 0.1 equiv) were placed in a Schlenk flask, which was purged with argon and then charged with pinacolborane (1.45 mL, 10.0 mmol, 10.0 equiv), Et_3N (1.49 mL), and dried 1,4-dioxane (4 mL). The mixture was stirred at reflux for 3 h under argon. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether = 1:4) and recrystallized from a mixture of dichloromethane and petroleum ether to give a white solid (158 mg, 36 % yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.67$ (s, 2H, carbazole), 7.91 (dd, $J = 8.2$, 0.9 Hz, 2H, carbazole), 7.40 (d, $J = 8.2$ Hz, 2H, carbazole), 4.38 (q, $J = 7.2$ Hz, 2H), 1.45–1.37 ppm (m, 27H).

*β,β′-Diboryl Zn^{II} Porphyrin **1***

5,10,15-*tris*(3,5-di-*tert*-butylphenyl) Zn^{II} porphyrin (938.7 mg, 1.0 mmol, 1.0 equiv), bis(pinacolato)diboron (2539.4 mg, 10.0 mmol, 10.0 equiv), 4,4′-di-tertbutyl-2,2′-bipyridyl (26.8 mg, 0.1 mmol, 0.1 equiv), and [Ir(OMe)(cod)]$_2$ (33.2 mg, 0.05 mmol, 0.05 equiv) were added to a Schlenk flask, which was evacuated and purged with argon five times, and then charged with dried 1,4-dioxane (13.0 mL). The resulting mixture was stirred at reflux for 72 h under argon. After removal of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2. The solution was filtered through a short column of silica gel to remove the catalyst and insoluble salts (eluent: CH_2Cl_2). Then, the solvent was removed under reduced pressure, and the residue was purified by recrystallization from a mixture of methanol and dichloromethane to afford β,β′-diboryl Zn^{II} porphyrin **1** as a dark red solid (978 mg, 82 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 11.45$ (s, 1H, *meso*), 9.73 (s, 2H, pyrrole-β), 8.98 (s, 4H, pyrrole-β), 8.07 (d, $J = 22.7$ Hz, 6H, Ar-*o*-H), 7.78 (d, $J = 11.8$ Hz, 3H, Ar-*p*-H), 1.71 (s, 24H), 1.55 (s, 36H, *tert*-butyl), 1.50 ppm (s, 18H, *tert*-butyl).

General Procedure for the Synthesis by the Suzuki–Miyaura Coupling Reaction

β,β′-Diboryl Zn^{II} porphyrin **1** (119.1 mg, 0.10 mmol, 1.0 equiv), bromo-substituted bridges (1–5 equiv), [$Pd_2(dba)_3$] (0.03 equiv), PPh_3 (0.12 equiv), Cs_2CO_3 (2.0 equiv), and CsF (2.0 equiv) were added to a Schlenk flask, which was purged with argon and then charged with dried toluene and DMF (2:1, 6 mL). The resulting mixture was thoroughly degassed through three freeze–pump–thaw cycles, and then stirred at 90 °C for 24 h under argon. The reaction was quenched with water and extracted with CH_2Cl_2, and the organic layer was dried over anhydrous sodium sulfate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel to afford the desired products.

*β,β′-Dicarbazole Zn^{II} Porphyrin **2***

It was prepared by the coupling reaction of **1** with 3,6-dibromo-9-ethylcarbazole (5.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:4) and recrystallization from 20 % methanol/CH_2Cl_2 to afford **2** as a red solid in 76 % yiled. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.83$ (s, 1H, *meso*), 9.21 (s, 2H, pyrrole-β), 9.06 (q, $J = 4.7$ Hz, 4H, pyrrole-β), 8.98 (s, 2H, carbazole), 8.56 (d, $J = 8.3$ Hz, 2H, carbazole), 8.29 (d, $J = 1.8$ Hz, 2H, carbazole), 8.21 (d, $J = 1.7$ Hz, 4H, Ar-H), 8.13 (d, $J = 1.7$ Hz, 2H, Ar-H), 7.83 (s, 2H, Ar-H), 7.80 (s, 1H, Ar-H), 7.74 (d, $J = 8.4$ Hz, 2H, carbazole), 7.59 (dd, $J = 8.7$, 1.9 Hz, 2H, carbazole), 7.32 (d, $J = 8.7$ Hz, 2H, carbazole), 4.37 (d, $J = 7.3$ Hz, 4H, ethyl), 1.60–1.49 (m, 54H, *tert*-butyl), 1.36 ppm (t, $J = 7.1$ Hz, 6H, ethyl); MS (MALDI-TOF): *m*/*z* calcd for $C_{90}H_{92}Br_2N_6Zn$: 1480.5 $[M]^+$; found: 1483.1.

*Carbazole-bridged Zn^{II} Porphyrin Array **3***

It was prepared by the coupling reaction of **1** with **2** (1.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:5) and recrystallization from 20 % methanol/CH_2Cl_2 to afford **3** as a red solid in 41 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.33$ (s, 2H, *meso*), 9.00 (s, 8H, pyrrole-β), 8.94 (s, 4H, pyrrole-β), 8.86 (s, 4H, carbazole), 8.15 (d, $J = 15.8$ Hz, 8H, Ar-H), 8.04 (s, 4H, Ar-H), 7.97 (d, $J = 9.2$ Hz, 4H, carbazole), 7.76 (s, 2H, Ar-H), 7.71 (s, 4H, Ar-H), 7.66 (d, $J = 8.4$ Hz, 4H, carbazole), 4.57 (m, $J = 7.0$ Hz, 4H, ethyl), 1.63 (t, $J = 7.1$ Hz, 6H, ethyl), 1.52–1.40 ppm (m, 108H, *tert*-butyl); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 150.65$, 150.07, 149.35, 148.85, 148.68, 148.59, 148.56, 147.52, 142.10, 141.98, 140.37, 132.70, 132.22, 131.93, 129.78, 129.11, 128.43, 123.66, 123.48, 122.63, 121.90, 120.85, 120.61, 104.73, 35.18, 35.10, 31.92, 31.85, 14.21 ppm; MS (MALDI-TOF): *m*/*z* calcd for $C_{152}H_{162}N_{10}Zn_2$: 2254.6 $[M]^+$; found 2258.2; elemental anal. calcd. (%) for $C_{152}H_{162}N_{10}Zn_2$: C 80.79, H 7.23, N 6.20; found: C 80.55, H 7.46, N 6.01.

*β,β′-Difluorene Zn^{II} Porphyrin **4***

It was prepared by the coupling reaction of **1** with 3,6-dibromo-9,9-pentylfluorene (5.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:6) and recrystallization from 20 % methanol/CH_2Cl_2 to afford **4** as a red solid in 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 10.92$ (s, 1H, meso), 9.25 (s, 2H, pyrrole-β), 9.06 (dd, $J = 11.9$, 4.7 Hz, 4H, pyrrole-β), 8.66 (s, 2H,fluorene), 8.39 (d, $J = 7.7$ Hz, 2H, fluorene), 8.21 (d, $J = 1.7$ Hz, 4H, Ar-o-H), 8.11 (d, $J = 1.7$ Hz,2H, Ar-o-H), 8.04 (d, $J = 1.7$ Hz, 2H, fluorene), 7.82 (dt, $J = 13.8$, 1.8 Hz, 3H, Ar-p-H), 7.68 (d, $J = 7.7$ Hz, 2H, fluorene), 7.51 (dd, $J = 8.1$, 1.8 Hz, 2H, fluorene), 7.32 (d, $J = 8.1$ Hz, 1H, fluorene), 2.06–1.98 (m, 8H), 1.59 (s, 36H, tert-butyl), 1.54 (s, 18H, *tert*-butyl), 1.11 (ddd, $J = 19.0$, 12.8, 5.8 Hz, 16H), 0.86 (s,8H), 0.76 ppm (t, *J*=7.0 Hz, 12 H); MS (MALDI-TOF): *m*/*z* calcd for $C_{108}H_{126}Br_2N_4Zn$: 1705.3 $[M]^+$; found: 1703.8.

Fluorene-bridged Zn^{II} Porphyrin Array 5

It was prepared by the coupling reaction of **1** with **4** (1.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:6) and recrystallization from 20% methanol/CH_2Cl_2 to afford **5** as a red solid in 38% yield. ^1H NMR (400 MHz, $CDCl_3$): δ=10.27 (s, 2 H, *meso*), 8.96 (dd, *J*=11.6, 5.4 Hz, 12 H, pyrrole-β), 8.47 (s, 4 H, fluorene), 8.17–7.92 (m, 12 H, Ar-H), 7.80 (d, *J*=8.6 Hz, 4 H, fluorene), 7.74 (d, *J*=6.6 Hz, 6 H, Ar-H), 7.66 (d, *J*=7.8 Hz, 4 H, fluorene), 2.21 (d, *J*=12.3 Hz, 4 H, pentyl), 2.04 (d, *J*=6.4 Hz, 4 H, pentyl), 1.52–1.40 (m, 108 H, *tert*-butyl), 1.27–1.17 (m, 24 H, pentyl), 0.86 ppm (d, *J*=7.5 Hz, 12 H, pentyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.47, 149.71, 149.09, 147.92, 147.72, 147.68, 147.61, 146.06, 140.93, 139.97, 135.36, 131.47, 131.25, 131.00, 128.99, 128.81, 122.59, 122.05, 121.70, 120.93, 119.86, 53.67, 34.19, 34.10, 31.71, 31.78, 30.90, 30.84, 28.86, 23.92, 21.57, 13.28 ppm; MS (MALDI-TOF): *m*/*z* calcd for $C_{170}H_{196}N_8Zn_2$: 2477.6 $[M]^+$; found: 2480.4; elemental anal. calcd. (%) for $C_{170}H_{196}N_8Zn_2$: C 82.26, H 7.96, N 4.51; found: C 82.01, H 8.10, N 4.36.

*β,β′-Difluorenone Zn^{II} Porphyrin **6***

It was prepared by the coupling reaction of **1** with 3,6-dibromofluorenone (5.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:6) and recrystallization from 20% methanol/CH_2Cl_2 to afford **6** as a red solid in 48% yield. ^1H NMR (400 MHz, $CDCl_3$): δ=10.69 (s, 1 H, *meso*), 9.30 (s, 2 H, pyrrole-β), 9.07 (dd, *J*=10.5, 4.7 Hz, 4 H, pyrrole-β), 8.42 (s, 2 H, fluorenone), 8.28 (d, *J*=7.5 Hz, 2 H, fluorenone), 8.18 (d, *J*=1.6 Hz, 4 H, Ar-H), 8.09 (d, *J*=1.5 Hz, 2 H, Ar-H), 8.03 (d, *J*=7.6 Hz, 2 H, fluorenone), 7.85 (dd, *J*=10.4, 8.6 Hz, 3 H, Ar-H), 7.51–7.41 (m, 6 H, fluorenone), 1.58 (s, 36 H, *tert*-butyl), 1.54 ppm (s, 18 H, *tert*-butyl); MS (MALDI-TOF): *m*/*z* calcd for $C_{88}H_{82}Br_2N_4O_2Zn$: 1453.1 $[M]^+$; found: 1450.4.

*Fluorenone-bridged Zn^{II} Porphyrin Array **7***

It was prepared by the coupling reaction of **1** with **6** (1.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:6) and recrystallization from 20% methanol/CH_2Cl_2 to afford **7** as a red solid in 22% yield. ^1H NMR (400 MHz, $CDCl_3$): δ=9.87 (s, 2 H, *meso*), 8.97 (d, *J*=8.7 Hz, 12 H, pyrrole-β), 8.20 (s, 4 H, fluorenone), 8.12 (s, 2 H, Ar-H), 8.05 (s, 4 H, Ar-H), 8.01 (s, 4 H, Ar-H), 7.97 (d, *J*=7.6 Hz, 4 H, fluorenone), 7.94 (s, 2 H, Ar-H), 7.80 (d, *J*=7.6 Hz, 4 H, fluorenone), 7.76 (s, 2 H, Ar-H), 7.74 (d, *J*=1.7 Hz, 4 H, Ar-H), 1.51–1.40 ppm (m, 108 H, *tert*-butyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.95, 150.58, 148.87, 148.82, 148.75, 148.71, 148.15, 145.25, 144.61, 144.41, 141.75, 141.46, 134.35, 132.68, 132.42, 132.17, 131.97, 129.90, 129.67, 124.54, 123.46, 123.35, 122.57, 121.16, 35.19, 35.10, 31.88, 31.83 ppm; MS (MALDI-TOF): *m*/*z* calcd for $C_{150}H_{152}N_8O_2Zn_2$: 2226.2 $[M]^+$; found: 2228.1; elemental anal. calcd. (%) for $C_{150}H_{152}N_8O_2Zn_2$: C 80.80, H 6.87, N 5.03; found: C 80.24, H 6.98, N 4.88.

*Carbazole-bridged Porphyrin Ring **8***

It was prepared by the coupling reaction of **2** with 3,6-dibory-9-ethylcarbazole (1.0 equiv) according to the general procedure and purified by column chromatography on silica gel (CH_2Cl_2/petroleum ether 1:6) and recrystallization from 20% methanol/CH_2Cl_2 to afford **8** as a red solid in 45% yield. ^1H NMR (400 MHz, $CDCl_3$): δ=10.68 (s, 1 H, *meso*), 9.06 (s, 4 H, pyrrole-β), 8.94 (s, 2 H, carbazole), 8.90 (s, 2 H, pyrrole-β), 8.62 (s, 2 H, carbazole), 8.18 (d, *J*=7.4 Hz, 3 H, Ar-H), 8.11 (s, 2 H, carbazole), 8.07 (d, *J*=7.0 Hz, 3 H, Ar-H), 8.02 (s, 2 H, carbazole), 7.82 (d, *J*=8.8 Hz, 3 H, Ar-H), 7.74 (s, 2 H, carbazole), 7.64 (d, *J*=8.4 Hz, 2 H, carbazole), 7.58 (d, *J*=7.6 Hz, 2 H, carbazole), 7.40 (d, *J*=8.4 Hz, 4 H, carbazole), 4.48 (q, *J*=6.9 Hz, 4 H, ethyl), 4.39 (q, *J*=6.9 Hz, 2 H, ethyl), 1.58–1.48 ppm (m, 63 H, *tert*-butyl and ethyl); ^{13}C NMR (100 MHz, $CDCl_3$): δ=150.67, 150.33, 148.72, 148.60, 148.32, 147.93, 147.64, 142.12, 142.03, 140.32, 139.95, 139.29, 138.16, 135.45, 134.62, 132.44, 132.08, 130.20, 129.78, 129.68, 129.51, 129.46, 126.49, 126.27, 124.83, 124.35, 123.49, 123.15, 122.39, 122.31, 121.85, 121.75, 120.93, 120.82, 108.77, 108.54, 107.77, 104.58, 38.57, 38.09, 35.21, 35.17, 31.94, 31.59, 29.86, 29.52, 14.42, 14.27, 14.11 ppm; MS (MALDI-TOF): *m*/*z* calcd for $C_{104}H_{103}N_7Zn$: 1515.6 $[M]^+$; found: 1514.8; elemental anal. calcd. (%) for $C_{104}H_{103}N_7Zn$: C 82.37, H 6.85, N 6.47; found: C 82.02, H 7.10, N 6.38.

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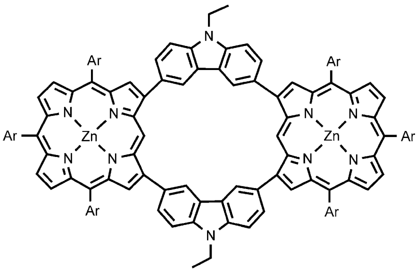
Do you cross the bridge or do you fade away: Doubly β-to-β bridged cyclic Zn^{II} porphyrin arrays with carbazole, fluorene, and fluorenone as bridges were constructed. The incorporation of bridge units with different electronic effects results in different photophysical properties of the cyclic Zn^{II} porphyrin arrays.



Porphyrinoids

Qingshan Hao, Yi Zeng, Tianjun Yu, Jinping Chen, Guoqiang Yang,* Yi Li** ——— ▮▮▮▮–▮▮▮▮

Synthesis and Photophysical Properties of Doubly β-to-β Bridged Cyclic Zn^{II} Porphyrin Arrays