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## **Electronic Supplementary Information**

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

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## **1. General Methods**

All chemicals were obtained from commercial suppliers and were used as received unless other-wise noted. All reactions were conducted with oven-dried glassware under atmosphere or nitrogen. Solvents were dried and distilled following usual protocols. Column chromatography was carried out using silica gel (200-300 mesh). Solvents for extraction and chromatography were reagent grade. CDCl<sub>3</sub> and CD<sub>2</sub>Cl<sub>2</sub> were from Cambridge Isotope Laboratories (CIL). Analytical NMR spectra were recorded on Bruker AVANCE AV II-400 MHz or AVANCE AV II-500 MHz, at a constant temperature of 298 K, if not specifically indicated. Chemical shifts are reported in  $\delta$  values in ppm using tetramethylsilane (TMS) or residual solvent as internal standard and coupling constants (J) are denoted in Hz. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, dd = doublet and m =multiplet. MALDI-TOF MS spectra were recorded on a Bruker Autoflex III MS and AXIMA Performance spectrometer, matrix is  $\alpha$ -cyano-4-hydroxycinnamic acid (CCA), 2,6-dihydroxyacetophenone (DHAP) and 2,5-dihydroxybenzoic acid (DHB). ESI mass spectra were recorded on a Bruker Daltonics MicroTOF-Q II. ESI-MS were obtained on a Thermo-ITQ. UV-vis spectra were measured by SHIMADZU UV-2700. EPR spectra were obtained using Bruker EMX10/12 X-band variable-temperature apparatus. Cyclic voltammetry (CV) measurements were performed in dry CH<sub>2</sub>Cl<sub>2</sub> on a CHI 620C electrochemical analyzer with a three-electrode cell, using 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte, AgCl/Ag as reference electrode, gold disk as working electrode, Pt wire as counter electrode, with scan rate of 20 mV/s for CV. Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Cary Eclipse fluorescence spectrophotometer.

### 2. Synthetic Protocols



Scheme S1. Synthetic route of macrocycle  $M_n$  (n = 4 - 7).

#### Synthesis of compound Cz-Ar

Under the protection of argon, carbazole (1.48 g, 8.82 mmol), compound 5-bromo-1,3-di-tert-butyl-2-methoxybenzene (2.40 g, 8.02 mmol), Pd(dba)<sub>2</sub> (922 mg, 1.60 mmol), P(*t*-Bu)<sub>3</sub>·HBF<sub>4</sub> (931 mg, 3.21 mmol), and sodium tert-butoxide (1.54 g, 16.0 mmol) were added into a dry Schlenk tube. Then 30 mL of dry toluene was added to disperse the powder. After that, the mixture was stirred at reflux for 24 h. After cooling to room temperature, undissolved solid was filtered. The filtrate was concentrated under reduced pressure to obtain the crude product, which was purified by column chromatography using petroleum ether:dichloromethane = 20:1 as the eluent to give pure compound **Cz-Ar** as a white solid (2.73 g, 80%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K)  $\delta$  (ppm): 8.17 (d, *J* = 7.8 Hz, 2H), 7.49 (s, 2H), 7.43 - 7.37 (m, 4H), 7.24 (m, 2H), 3.82 (s, 3H), 1.50 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K)  $\delta$  (ppm): 159.3, 146.1, 141.7, 132.9, 126.8, 125.8, 124.0, 121.0, 120.5, 110.5, 65.0, 36.7, 32.3. HR-ESI-TOF MS: m/z = 386.2467 (calculated for C<sub>27</sub>H<sub>32</sub>NO: 385.2484 [M+H]<sup>+</sup>).

#### Synthesis of compound diBrCz-Ar

Under the protection of argon, compound **Cz-Ar** (2.00 g, 5.19 mmol) was added into a dry Schlenk tube. Then 30 mL of dry DMF was added to disperse the powder. After cooling to 0°C, NBS (2.31 g, 13.0 mmol) was added to the solution. In the dark conditions, the mixture was stirred at room temperature for 8 h. The reaction was washed with EA and H<sub>2</sub>O three times. The organic layer was concentrated under reduced pressure. the crude product was purified by column chromatography using petroleum ether:dichloromethane = 50:1 as the eluent to give pure compound **diBrCz-Ar** as a white solid (2.67 g, 95%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K)  $\delta$  (ppm): 8.22 (d, *J* = 1.9 Hz, 2H), 7.53 (dd, *J*<sub>1</sub> = 8.7 Hz, *J*<sub>2</sub> = 1.9 Hz, 2H), 7.37 (s, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 1.47 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>COCD<sub>3</sub>, 298 K) δ (ppm): 159.4, 146.1, 140.5, 131.5, 129.7, 125.3, 124.0, 123.5, 112.9, 112.1, 64.9, 36.4, 32.2. HR-ESI-TOF MS: m/z = 544.0690 (calculated for C<sub>27</sub>H<sub>30</sub>NOBr<sub>2</sub>: 544.0674 [M+H]<sup>+</sup>).

#### Synthesis of compound $M_n$

Bis[1,5-cyclooctanediene]nickel(0) (Ni[COD]<sub>2</sub>, 1.00 g, 3.64 mmol), cis-1,5cyclooctanediene (0.629 g, 5.82 mmol) and 2,2'-bipyridine (0.727 g, 4.65 mmol) were added into a dry Schlenk tube. Then 30 mL of dry Toluene was added to disperse the powder. Under the protection of argon, the suspension was stirred at 80°C for 30 min to form the nickel catalyst complex, which was dark purple. After that, a solution of **diBrCz-Ar** (0.790 g, 1.45 mmol) in 30 mL of DMF was injected dropwise. Four days later, the reaction was quenched with 10.0 mL of aqueous HCl and extracted with dichloromethane. The organic layer was concentrated under reduced pressure. The residue was passed through a pad of silica gel (eluent: PE:  $CH_2Cl_2 = 5:1$ ) and purified successively by GPC.

*M*<sub>4</sub>: white solid (155 mg, 28 %), <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K)  $\delta$  (ppm): 9.00 (d, *J* = 1.4 Hz, 2H), 7.95 (dd, *J*<sub>1</sub> = 8.6 Hz, *J*<sub>2</sub> =1.7 Hz, 2H), 7.62-7.59 (m, 4H), 3.87 (s, 3H), 1.56 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K)  $\delta$  (ppm): 158.9, 145.8, 141.1, 133.9, 132.6, 125.3, 125.2, 124.8, 119.0, 110.8, 64.9, 36.5, 32.3. LR-MALDI-TOF MS: m/z = 1533.9 (calculated for C<sub>108</sub>H<sub>116</sub>N<sub>4</sub>O<sub>4</sub>: 1533.9). HR-MALDI-TOF MS: m/z = 1533.9120 (calculated for C<sub>108</sub>H<sub>116</sub>N<sub>4</sub>O<sub>4</sub>: 1533.9030).

*M*<sub>5</sub>: white solid (83.4 mg, 15 %), <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): 8.56 (d, J = 1.4 Hz, 2H), 7.70 (dd,  $J_1 = 8.6$  Hz,  $J_2 = 1.7$  Hz, 2H), 7.56 (m, 4H), 3.85 (s, 3H), 1.54 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) δ (ppm): 159.1, 145.9, 141.1, 135.5, 132.4, 127.9, 125.6, 124.0, 119.3, 110.6, 64.9, 36.5, 32.3. LR-MALDI-TOF MS: m/z = 1917.4 (calculated for C<sub>135</sub>H<sub>145</sub>N<sub>5</sub>O<sub>5</sub>: 1917.1). HR-MALDI-TOF MS: m/z = 1917.1168 (calculated for C<sub>135</sub>H<sub>145</sub>N<sub>5</sub>O<sub>5</sub>: 1917.1249).

*M*<sub>6</sub>: white solid (11.1 mg, 2 %), <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): 8.34 (d, J = 1.0 Hz, 2H), 7.59 (dd,  $J_1 = 8.5$  Hz,  $J_2 = 1.6$  Hz, 2H), 7.46 - 7.40 (m, 4H), 3.73 (s, 3H), 1.41 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) δ (ppm): 157.7, 144.6, 139.8, 134.1, 131.4, 125.7, 124.2, 122.8, 118.7, 109.2, 63.7, 35.3, 31.1. LR-MALDI-TOF MS: m/z = 2300.6 (calculated for C<sub>162</sub>H<sub>174</sub>N<sub>6</sub>O<sub>6</sub>: 2300.3). HR-MALDI-TOF MS: m/z = 2300.3504 (calculated for C<sub>162</sub>H<sub>174</sub>N<sub>6</sub>O<sub>6</sub>: 2300.3528).

*M*<sub>7</sub>: white solid (5.50 mg, 1 %), <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) δ (ppm): δ 8.34 (d, J = 0.9 Hz, 2H), 7.59 (dd,  $J_1 = 8.4$  Hz,  $J_2 = 1.1$  Hz, 2H), 7.47 - 7.41 (m, 4H), 3.73 (s, 3H), 1.42 (s, 18H). <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298K) δ (ppm): 157.7, 144.6, 139.8, 134.2, 131.5, 125.4, 124.1, 123.1, 118.8, 109.2, 63.7, 35.3, 31.1. LR-MALDI-TOF MS: m/z = 2684.9 (calculated for C<sub>189</sub>H<sub>203</sub>N<sub>7</sub>O<sub>7</sub>: 2684.6). HR-MALDI-TOF MS: m/z = 2684.5809 (calculated for C<sub>189</sub>H<sub>203</sub>N<sub>7</sub>O<sub>7</sub>: 2684.5811).

### Synthesis of compound (diBrCz-Ar)<sub>2</sub>•DDQ

Under the protection of argon, **diBrCz-Ar** (20.0 mg,  $3.68 \times 10^{-5}$  mmol) and DDQ (16.7 mg,  $7.36 \times 10^{-5}$  mmol) were added into a dry Schlenk tube. Then 5.0 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added to disperse the powder. After that, the mixture was stirred for 2 h at room temperature.

### Synthesis of compound $M_4SbF_6$

Under the protection of argon,  $M_4$  (20.0 mg,  $1.30 \times 10^{-5}$  mmol) and AgSbF<sub>6</sub> (4.5 mg,  $1.30 \times 10^{-5}$  mmol) were added into a dry Schlenk tube. Then 5.0 mL of dry CH<sub>2</sub>Cl<sub>2</sub> was added to disperse the powder. After that, the mixture was stirred for 30 min at room temperature.

#### Synthesis of compound $C_4$ - $M_n$

The synthesis of compound  $C_4$ - $M_n$  (n =4 - 7) was according to previous report.<sup>S1</sup>



Scheme S2. Synthetic route of macrocycle  $C_4$ - $M_n$  (n = 4 - 7).



Fig. S1. The GPC trace (CH<sub>2</sub>Cl<sub>2</sub>, flow rate = 10 mL/min) for C<sub>4</sub>-M<sub>n</sub> (n = 4 - 7).

# 3. Cyclic voltammetry



**Fig. S2**. Cyclic voltammograms of **diBrCz-Ar** (blue line) and **diBrCz-C4** (red-line) measured in CH<sub>2</sub>Cl<sub>2</sub> containing 0.1 M *n*Bu<sub>4</sub>NPF<sub>6</sub> at 298 K.



Fig. S3. Cyclic voltammograms of  $M_4$  measured in  $CH_2Cl_2$  containing 0.1 M  $nBu_4NPF_6$  at 298 K.

compound	$E_{1/2}$	$E_{ox}^{onset}$	IPa
diBrCz-C4	+ 0.94 V	+1.19 V	5.35 eV
diBrCz-Ar	+ 1.10 V	+ 1.16 V	5.26 eV
M4	+ 0.22 V, +0.35 V, +0.62 V, +0.78 V	+ 0.16 V	4.66 eV

Table S1. Summary of the electrochemical data.

<sup>a</sup>IP = -  $(4.5 + \frac{E_{ox}^{onset}}{ox})$  ev<sup>S2</sup>

# 4. Stability of diBrCz-Ar<sup>++</sup> and M<sub>4</sub><sup>++</sup>



Fig. S4. UV-vis-NIR spectra of (diBrCz-Ar)<sub>2</sub>•DDQ in CH<sub>2</sub>Cl<sub>2</sub> at different time.



Fig. S5. UV-vis-NIR spectra of  $M_4^{++} \cdot SbF_6^-$  in  $CH_2Cl_2$  at different time.

## **5** Theoretical calculation

#### 5.1 Molecular modeling of M<sub>n</sub>

Geometries of macrocycles  $M_n$  (n = 4 - 7) were optimized at RB3LYP/6-311G(d,p) level of theory followed by frequency calculations to confirm the stationary points. All calculations were performed by the Gaussian 09 software package.<sup>S3</sup>



Fig. S6. Chemical structure of  $M_4$  (a) and its view of geometry (b and c) optimized by RB3LYP/6-311G(d,p) level of theory (all *t*-butyl were replaced by methyl to reduce the computational cost).



Fig. S7. Chemical structure of  $M_5$  (a) and its view of geometry (b and c) optimized by RB3LYP/6-311G(d,p) level of theory (all *t*-butyl were replaced by methyl to reduce the computational cost).



**Fig. S8**. Chemical structure of  $M_6$  (a) and its view of geometry (b and c) optimized by RB3LYP/6-311G(d,p) level of theory (all *t*-butyl were replaced by methyl to reduce the computational cost).



Fig. S9. Chemical structure of  $M_7$  (a) and its view of geometry (b and c) optimized by RB3LYP/6-311G(d,p) level of theory (all *t*-butyl were replaced by methyl to reduce the computational cost).

## 5.2 Molecular modeling of diBrCz-C4 and diBrCz-C4+



**Fig. S10**. Chemical structure (a) and (d), spin density (b) and (e), and Mulliken atomic spin density values (c) and (f) of radical cation **diBrCz-C4**<sup>•+</sup> and **diBrCz-Ar**<sup>•+</sup> at the UB3LYP/6-311G(d,p) level of theory.

## 5.3 Molecular modeling of M<sub>4</sub><sup>++</sup>



Fig. S11. Chemical structure (a), optimized geometry (b), and spin density map (c) of  $M_4^{++}$  at the UB3LYP/6-311G(d,p) level of theory.

## 6 Host-guest interaction of M<sub>n</sub> and fullerene

#### 6.1 Fluorescence titration

To determine the stoichiometry and association constant between  $M_5$  and  $C_{60}$ , fluorescence titrations were done with solutions which had a constant concentration of  $M_5$  (2.0 × 10<sup>-5</sup> M) and varying concentrations of  $C_{60}$ . By a non-linear curve-fitting method, the association constant ( $K_a$ ) of  $M_5 \supset C_{60}$  was estimated to be (8.38 ± 0.33) × 10<sup>4</sup> M<sup>-1</sup>.

The non-linear curve-fitting was based on the equation:  $\Delta F = (\Delta F_{\infty} / [\mathbf{M}_{5}]_{0}) \times (0.5[C_{60}]_{0} + 0.5([\mathbf{M}_{5}]_{0} + 1/K_{a}) - (0.5 ([C_{60}]_{0}^{2} + (2[C_{60}]_{0}(1/K_{a} - [\mathbf{M}_{5}]_{0})) + (1/K_{a} + [\mathbf{M}_{5}]_{0})^{2})^{0.5}))^{S4}$ 

Where  $\Delta F$  is the change of emission intensity at  $[\mathbf{M}_5]_0$ ,  $\Delta \delta_{\infty}$  is the change of emission intensity when the host is completely complexed,  $[\mathbf{M}_5]_0$  is the fixed initial concentration of the host, and  $[C_{60}]_0$  is the initial concentration of  $C_{60}$ .



**Fig. S12**. Fluorescence spectral (excitation wavelength = 350 nm) changes of  $M_5$  (2.0 × 10<sup>-5</sup> M) on addition of C<sub>60</sub> (0 - 6.0 × 10<sup>-5</sup> M) in toluene at 298 K.



Fig. S13. Determination of the binding constant of  $M_5 \supset C_{60}$  in toluene at 298 K. Fitting result based on plot of emission intensity of  $M_5$  at 415 nm.

To determine the stoichiometry and association constant between  $M_5$  and  $C_{70}$ , fluorescence titrations were done with solutions which had a constant concentration of  $M_5$  (2.0 × 10<sup>-5</sup> M) and varying concentrations of  $C_{70}$ . By a non-linear curve-fitting method, the association constant ( $K_a$ ) of  $M_5 \supset C_{70}$  was estimated to be (7.64 ± 0.26) × 10<sup>4</sup> M<sup>-1</sup>.



**Fig. S14**. Fluorescence spectral (excitation wavelength = 350 nm) changes of  $M_5$  (2.0 × 10<sup>-5</sup> M) on addition of  $C_{70}$  (0 - 6.0 × 10<sup>-5</sup> M) in toluene at 298 K.



**Fig. S15**. Determination of the binding constant of  $M_5 \supset C_{70}$  in toluene at 298 K. Fitting result based on plot of emission intensity of  $M_5$  at 415 nm.

#### 6.2 Job's plot of M<sub>5</sub>⊃fullerene



**Fig. S16**. Fluorescence spectra (excitation wavelength = 350 nm) of  $M_5$  and  $C_{60}$  with different molar ratios when the total concentrations of  $M_5$  and  $C_{60}$  were fixed at  $1.0 \times 10^{-5}$  M in toluene (left) and Job's plot for  $M_5$  and  $C_{60}$  (right).



**Fig. S17**. Fluorescence spectra (excitation wavelength = 350 nm) of  $M_5$  and  $C_{70}$  with different molar ratios when the total concentrations of  $M_5$  and  $C_{70}$  were fixed at  $1.0 \times 10^{-5}$  M in toluene (left) and Job's plot for  $M_5$  and  $C_{70}$  (right).

## 6.3 Charge transfer band



**Fig. S18**. UV-vis spectral of  $\mathbf{M}_5$  (5.0 × 10<sup>-5</sup> M, black line),  $\mathbf{M}_5 \supset C_{60}$  (5.0 × 10<sup>-5</sup> M, blue line), and  $C_{60}$  (5.0 × 10<sup>-5</sup> M, yellow line) in toluene at 298 K.

## 6.4 MS of complex



Fig. 19. LR-MALDI-TOF MS of compound  $M_5 \supset C_{60}$ .



Fig. 20. LR-MALDI-TOF MS of compound  $M_5 \supset C_{70}$ .

#### 6.5 Molecular modeling of M<sub>5</sub> and fullerene

Geometries of host-guest complex were optimized at RB3LYP-D3/6-311+G(d,p) level of theory with BESS correction as well as frequency calculations to confirm the stationary points. All calculations were performed by the Gaussian 09 software package.<sup>S3</sup>



**Fig. S21**. Top view (a) and side view (b) of optimized geometry of  $M_5 \supset C_{60}$  at the RB3LYP-D3/6-311+G(d,p) level of theory.



**Fig. S22**. Top view (a) and side view (b) of optimized geometry of  $M_5 \supset C_{70}$  at the RB3LYP-D3/6-311+G(d,p) level of theory.

# 7 X-ray crystal data

## 7.1 X-ray crystal data of diBrCz-Ar

X-ray crystallography of single crystal obtained by slow evaporation solutions of **diBrCz-Ar** (2 mg) in CHCl<sub>3</sub> (1 mL) for 2 days. CCDC number: 2073892.



Fig. S23. X-ray crystal structure of diBrCz-Ar with top (left) and side views (right).

Identification code	exp_1861
Empirical formula	C <sub>27</sub> H <sub>29</sub> Br <sub>2</sub> NO
Formula weight	543.33
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /c
a/Å	8.7418(2)
b/Å	40.2906(7)
c/Å	14.2849(2)
α/°	90
β/°	103.339(2)
γ/°	90
Volume/Å <sup>3</sup>	4895.58(16)
Z	8
$\rho_{calc}g/cm^3$	1.474
μ/mm <sup>-1</sup>	4.334
F(000)	2208.0
Crystal size/mm <sup>3</sup>	$0.44 \times 0.38 \times 0.32$
Radiation	$CuK\alpha \ (\lambda = 1.54184)$

Table S2. Crystal data and structure refinement for	or <b>diBrCz-Ar</b> .
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$2\Theta$ range for data collection/°	6.728 to 134.158
Index ranges	$-10 \le h \le 9, -48 \le k \le 47, -17 \le l \le 17$
Reflections collected	49730
Independent reflections	$8703 [R_{int} = 0.1220, R_{sigma} = 0.0545]$
Data/restraints/parameters	8703/210/573
Goodness-of-fit on F <sup>2</sup>	1.064
Final R indexes [I>=2 $\sigma$ (I)]	$R_1 = 0.0758, wR_2 = 0.1963$
Final R indexes [all data]	$R_1 = 0.0784, wR_2 = 0.1988$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.89/-1.47

## 7.2 X-ray crystal data of (diBrCz-Ar)<sub>2</sub>•DDQ

X-ray crystallography of single crystal obtained by slow evaporation solutions of (diBrCz-Ar)<sub>2</sub>•DDQ (10 mg) in CH<sub>2</sub>Cl<sub>2</sub> (1 mL). CCDC number: 2071725.



Fig. S24. X-ray crystal structure of (diBrCz-Ar)<sub>2</sub>•DDQ with top and side views.



Fig. S25. The bond length of DDQ anion in (diBrCz-Ar)<sub>2</sub>•DDQ.

Identification code	exp_1755
Empirical formula	$C_{31}H_{29}Br_2ClN_2O_2$
Formula weight	656.83
Temperature/K	170.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.5868(5)

Table S3. Crystal data and structure refinement for (diBrCz-Ar)<sub>2</sub>•DDQ.

b/Å	10.6482(6)
c/Å	13.8870(6)
α/°	107.508(5)
β/°	104.966(4)
γ/°	94.584(4)
Volume/Å <sup>3</sup>	1421.06(13)
Z	2
$\rho_{calc}g/cm^3$	1.535
μ/mm <sup>-1</sup>	4.729
F(000)	664.0
Crystal size/mm <sup>3</sup>	$0.26 \times 0.22 \times 0.16$
Radiation	$CuK\alpha (\lambda = 1.54184)$
$2\Theta$ range for data collection/°	9.46 to 134.154
Index ranges	$-12 \le h \le 9, -12 \le k \le 12, -16 \le l \le 16$
Reflections collected	13645
Independent reflections	5043 [ $R_{int} = 0.0875$ , $R_{sigma} = 0.0929$ ]
Data/restraints/parameters	5043/114/377
Goodness-of-fit on F <sup>2</sup>	1.020
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.0700, wR_2 = 0.1778$
Final R indexes [all data]	$R_1 = 0.0943, WR_2 = 0.1922$
Largest diff. peak/hole / e Å <sup>-3</sup>	1.29/-0.93

## 7.3 X-ray crystal data of $M_4$

X-ray crystallography of single crystal obtained by vapor diffusion of MeOH (2 mL) into solutions of  $M_4$  (2 mg) in CHCl<sub>3</sub> (1 mL). CCDC number: 2071727.



Fig. S26. X-ray crystal structure of  $M_4$  with top and side views.

Identification code	MLJ_H4_0m
Empirical formula	$C_{108}H_{116}N_4O_4$
Formula weight	1534.04
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	26.709(3)
b/Å	24.342(3)
c/Å	20.0808(16)
α/°	90
β/°	113.763(2)
γ/°	90
Volume/Å <sup>3</sup>	11948.8(19)
Z	4
$\rho_{calc}g/cm^3$	0.853
μ/mm <sup>-1</sup>	0.071
F(000)	3296.0
Crystal size/mm <sup>3</sup>	$0.26 \times 0.18 \times 0.16$
Radiation	$\lambda = 0.82704$
20 range for data collection/°	3.878 to 62.476
Index ranges	$-32 \le h \le 28, -29 \le k \le 28, -20 \le l \le 22$
Reflections collected	38346
Independent reflections	10295 [ $R_{int} = 0.1002, R_{sigma} = 0.1087$ ]
Data/restraints/parameters	10295/334/537
Goodness-of-fit on F <sup>2</sup>	1.086
Final R indexes [I>=2σ (I)]	$R_1 = 0.1790, wR_2 = 0.3630$
Final R indexes [all data]	$R_1 = 0.2529, wR_2 = 0.3894$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.56/-0.64

Table S4. Crystal data and structure refinement for  $M_4$ .

## 7.4 X-ray crystal data of M<sub>5</sub>

X-ray crystallography of single crystal obtained by vapor diffusion of MeOH (2 mL) into solutions of  $M_5$  (2 mg) in CHCl<sub>3</sub> (1 mL). CCDC number: 2071729.



Fig. S27. X-ray crystal structure of  $M_5$  with top and side views.

2	5
Identification code	MLJ_H4_0m
Empirical formula	$C_{108}H_{116}N_4O_4$
Formula weight	1534.04
Temperature/K	273.15
Crystal system	monoclinic
Space group	C2/c
a/Å	26.709(3)
b/Å	24.342(3)
c/Å	20.0808(16)
α/°	90
β/°	113.763(2)
γ/°	90
Volume/Å <sup>3</sup>	11948.8(19)
Z	4
$\rho_{calc}g/cm^3$	0.853
μ/mm <sup>-1</sup>	0.071
F(000)	3296.0
Crystal size/mm <sup>3</sup>	$0.26\times0.18\times0.16$
Radiation	$\lambda = 0.82704$
2\Theta range for data collection/°	3.878 to 62.476
Index ranges	$-32 \le h \le 28, -29 \le k \le 28, -20 \le l \le 22$
Reflections collected	38346
Independent reflections	10295 [ $R_{int} = 0.1002, R_{sigma} = 0.1087$ ]
Data/restraints/parameters	10295/334/537

Table S5. Crystal data and structure refinement for M<sub>5</sub>.

Goodness-of-fit on F <sup>2</sup>	1.086
Final R indexes [I>= $2\sigma$ (I)]	$R_1 = 0.1790, wR_2 = 0.3630$
Final R indexes [all data]	$R_1 = 0.2529, wR_2 = 0.3894$
Largest diff. peak/hole / e Å <sup>-3</sup>	0.56/-0.64

## 8 Characterization of compound



Fig. S29. The <sup>13</sup>C NMR (100 MHz, 298 K) spectrum of compound Cz-Ar in CD<sub>3</sub>COCD<sub>3</sub>.



Fig. S30. HR-ESI-TOF MS of compound Cz-Ar.



Fig. S31. The <sup>1</sup>H NMR (400 MHz, 298 K) spectrum of compound diBrCz-Ar in CD<sub>2</sub>Cl<sub>2</sub>.



Fig. S32. The <sup>13</sup>C NMR (100 MHz, 298 K) spectrum of compound diBrCz-Ar in CD<sub>2</sub>Cl<sub>2</sub>.



Fig. S33. HR-ESI-TOF MS of compound diBrCz-Ar.



Fig. S35. The  ${}^{13}$ C NMR (100 MHz, 298 K) spectrum of compound  $M_4$  in  $CD_2Cl_2$ .



Fig. S36. LR-MALDI-TOF MS of compound M4.



Fig. S37. HR-MALDI-TOF MS of compound M4.



Fig. S38. 2D COSY (500 MHz, 298 K) spectrum of compound M<sub>4</sub> in CD<sub>2</sub>Cl<sub>2</sub>.



Fig. S39. 2D NOESY (500 MHz, 298 K) spectrum of compound  $M_4$  in  $\text{CD}_2\text{Cl}_2$ .



Fig. S41. The  ${}^{13}C$  NMR (100 MHz, 298 K) spectrum of compound  $M_5$  in  $CD_2Cl_2$ .



Fig. S42. LR-MALDI-TOF MS of compound M<sub>5</sub>.



Fig. S43. HR-MALDI-TOF MS of compound M<sub>5</sub>.



Fig. S44. 2D COSY (500 MHz, 298 K) spectrum of compound M<sub>5</sub> in CD<sub>2</sub>Cl<sub>2</sub>.



Fig. S45. 2D NOESY (500 MHz, 298 K) spectrum of compound  $M_5$  in  $CD_2Cl_2$ .



Fig. S47. The <sup>1</sup>H NMR (100 MHz, 298 K) spectrum of compound  $M_6$  in  $CD_2Cl_2$ .



Fig. S48. LR-MALDI-TOF MS of compound M<sub>6</sub>.



Fig. S49. HR-MALDI-TOF MS of compound M<sub>6</sub>.



Fig. S51. The <sup>1</sup>H NMR (100 MHz, 298 K) spectrum of compound  $M_7$  in  $CD_2Cl_2$ .



Fig. S52. LR-MALDI-TOF MS of compound M<sub>7</sub>.



Fig. S53. HR-MALDI-TOF MS of compound M<sub>7</sub>.

## 9 Reference

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