Supporting information

Self-assembled star-shaped aza-BODIPY mesogen affords white-light emission

Chao Liu, ‡ [a] Wei Ding, ‡ [a] Yuantao Liu,[a] Hongmei Zhao,[a] Xiaohong Cheng*[a,b]

[a] Key Laboratory of Medicinal Chemistry for Natural Resources, Chemistry School of Chemical Science and Technology, Yunnan University, Kunming, 650091, PR China.

[b] School of Chemistry and Chemical Engineering, Yangtze Normal University, Fuling, 408100, PR China.

Fax: (+86) 871 65032905

E-mail: xhcheng@ynu.edu.cn

‡Both authors contributed equally to this work

Content

1 Additional Experimental Data

1.1 Additional DSC traces

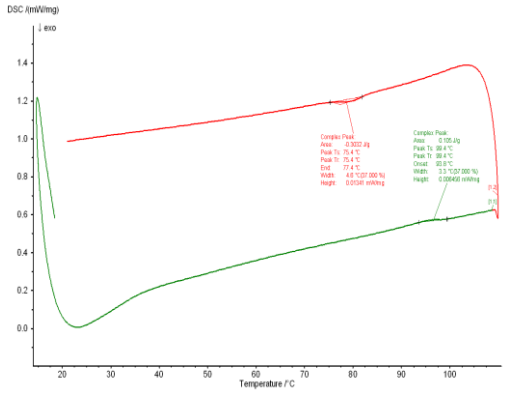


Fig. S1 DSC heating and cooling scans (10 K min^{-1}) of compound **ADP/12**.

Table S1 Experimental and calculated *d*-spacings of the observed SAXS reflections of the hexagonal phase in compound **ADP/12** at 55 °C. All intensity values are Lorentz and multiplicity corrected.

(*hk*)	$d_{obs.}$ –spacing (nm)	$d_{cal.}$ –spacing (nm)	*intensity*
(10)	3.75	3.76	100
(11)	2.17	2.17	0.02
(20)	1.88	1.88	0.05
a_{hex} = 4.34 nm			

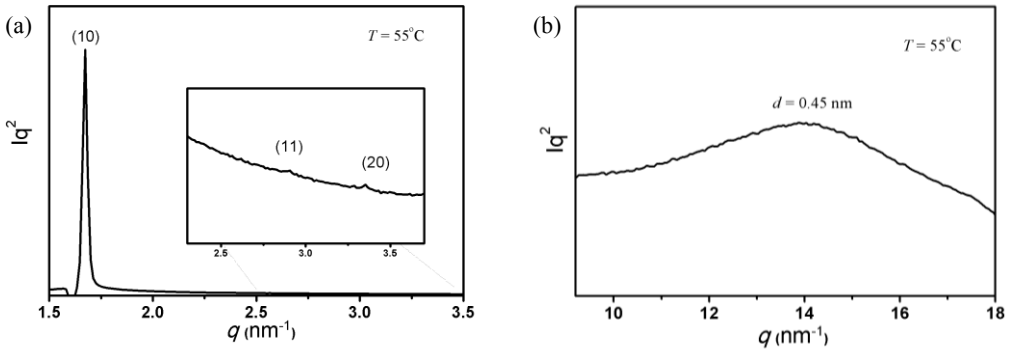


Fig. S2 (a) SAXS diffraction pattern of Col$_{hex}$/*p6mm* phase of compound **ADP/12** recorded at 55 °C; (b) Diffuse scattering in the wide-angle region of the Col$_{hex}$/*p6mm* phase of compound **ADP/12** at 55 °C.

Table S2 Calculations of molecular volume (V_{mol}), volume of the (hypothetical) unit cells(V_{cell}) and number of molecules in these unit cells (n_{cell}).[a]

Comp	phase	a/nm (T/°C)	V_{cell}/nm^3	V_{mol}/nm^3	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell}	n
ADP/12	Col_{hex}/*p6mm*	4.34 (55)	7.34	5.438	1.3	1.0	1.2	1.3

[a] V_{cell} = volume of the unit cell defined by the dimensions $1/2\ 3^{1/2}\ a^2\ h$ for the columnar phases; V_{mol} = volume for a single molecule as calculated using the crystal volume increments,[S1] $n_{cell,cryst}$ = number of molecules in the unit cell, calculated according to $n_{cell,cryst} = V_{cell}/V_{mol}$ (average packing coefficient in the crystal is $k = 0.7$;[S2] $n_{cell,liq}$ = number of molecules in the unit cell of an isotropic liquid with an average packing coefficient $k = 0.55$, calculated according to $n_{cell,liq} = 0.55/0.7 \times n_{cell,cryst}$; n_{cell} (average) = number of molecules in the unit cell in the cubic phase estimated as the average of that in the $n_{cell,cryst}$ and $n_{cell,liq}$.

Table S3 The phase transition temperatures, XRD data and other data of compound **ADP/12**.[a]

Comp.	T/°C [ΔH/kJ mol^{-1}]	a/nm (T/°C)	L	μ	d_{diff}
ADP/12	Cr 20 > Col_{hex}/*p6mm* 81.5 [0.4] Iso	a_{hex} = 4.34 (55)	6.8 nm	1.3	0.45 nm

a: Abbreviations: Cr = crystal; Col_{hex} = hexagonal columnar phase; Iso = isotropic liquid; a = lattice parameter; L = maximum molecular length in the most extended conformation; μ= number of molecules in a stratum of the columns in the Col_{hex} phase with a height corresponding to d_{diff}.

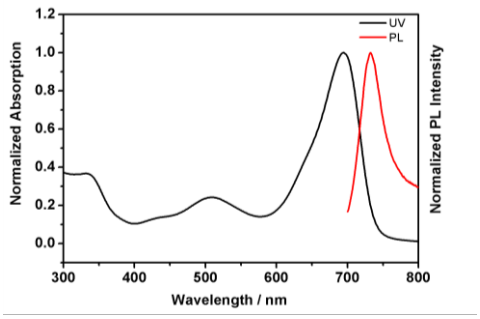


Fig. S3. The spectral of the **ADP/12** absorbance (black line) and emission (red line).

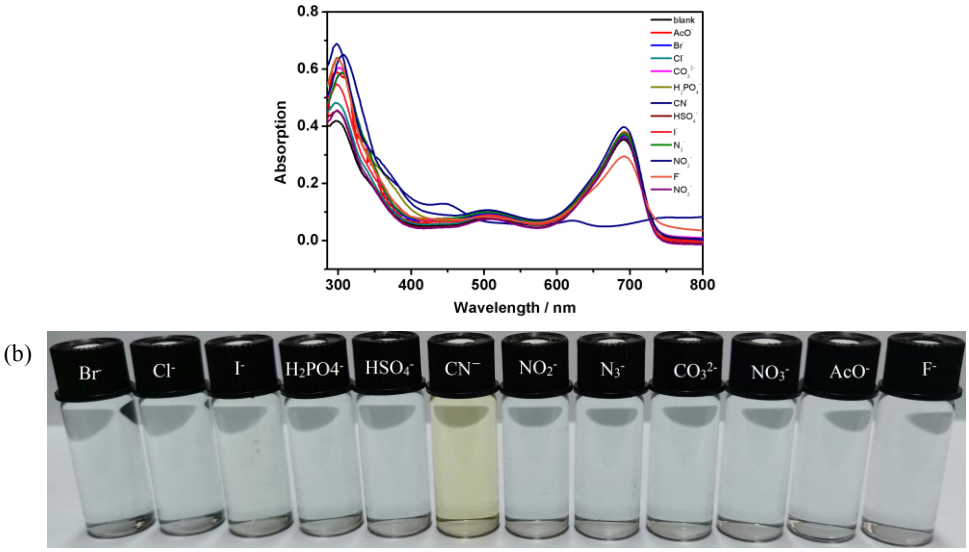


Fig. S4. (a) The absorption response of **ADP/12** (1×10^{-5} M) upon addition of different anions in THF at room temperature; (b) The samples with addition of different metal ions, under irradiation with daylight.

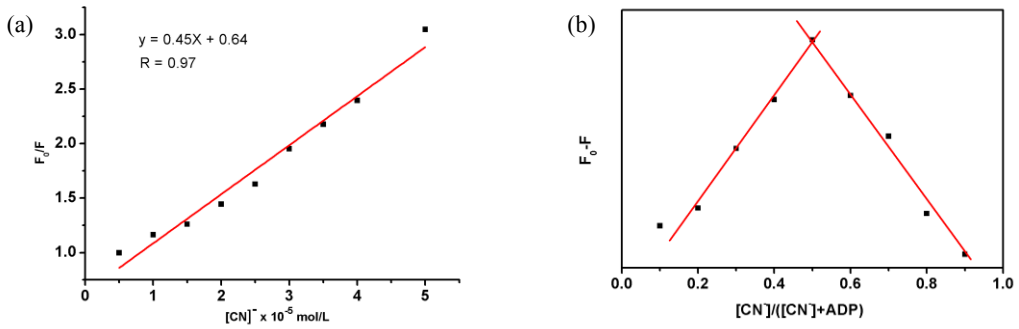


Fig. S5. Plots of the detection limits for CN^- evaluated from the fluorescence emission of **ADP/12**, Job's plots for **ADP/12-CN**$^-$, [**ADP/12**] + [CN^-] = 5.0 × 10^{-5} mol·L^{-1}, abbreviation: F_0 = the fluorescence emission maximum of the blank sample; F = the fluorescence emission maximum of samples after addition of CN^-.

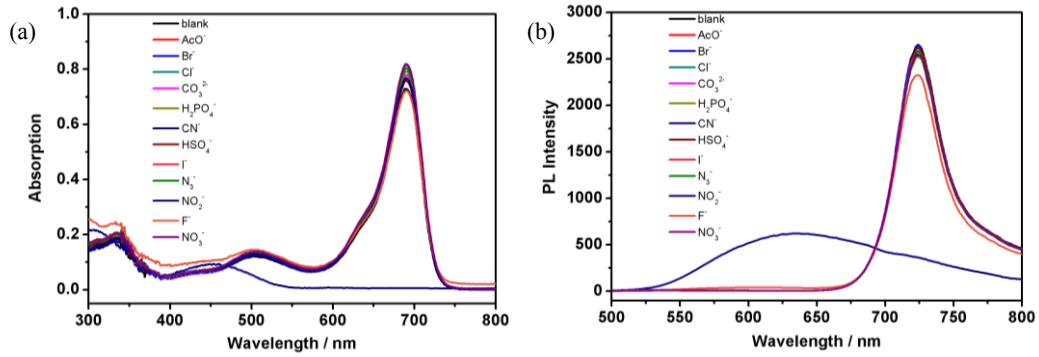


Fig. S6. The spectrum response of compound **6** (1 × 10^{-5} M) upon addition of different anions in THF at room temperature: (a) UV-vis absorption spectrum; (b) Fluorescence emission spectrum.

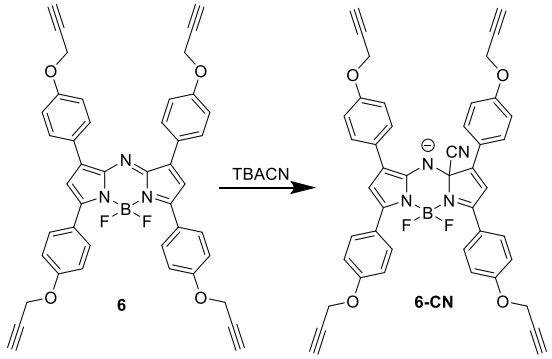


Fig. S7. Formation of **6-CN** by nucleophilic addition of CN^- ion to **6**.

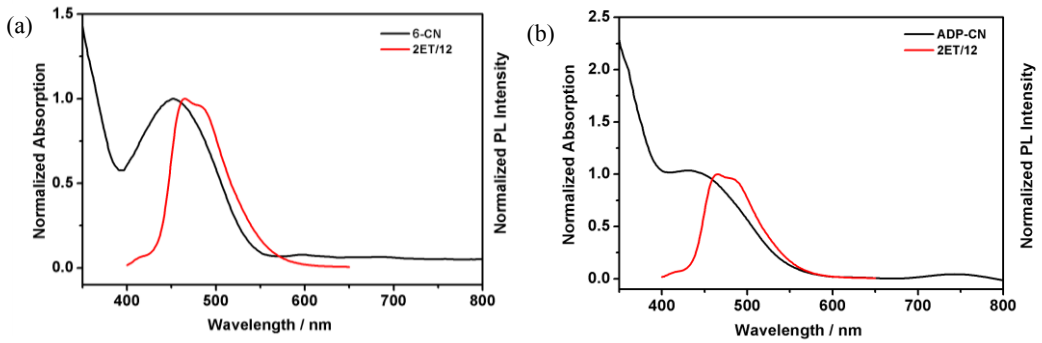


Fig. S8. (a) The spectral overlap between the **2ET/12** emission (red) and **6-CN** absorbance (black); (b) The spectral overlap between the **2ET/12** emission (red) and **ADP-CN** absorbance (black).

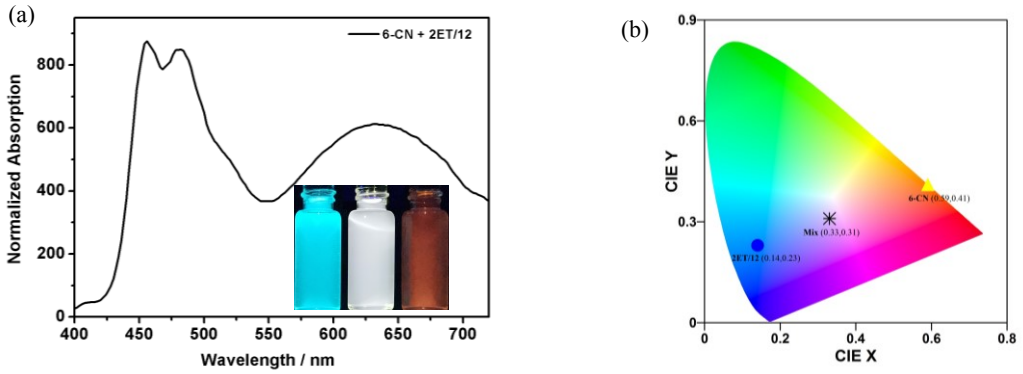
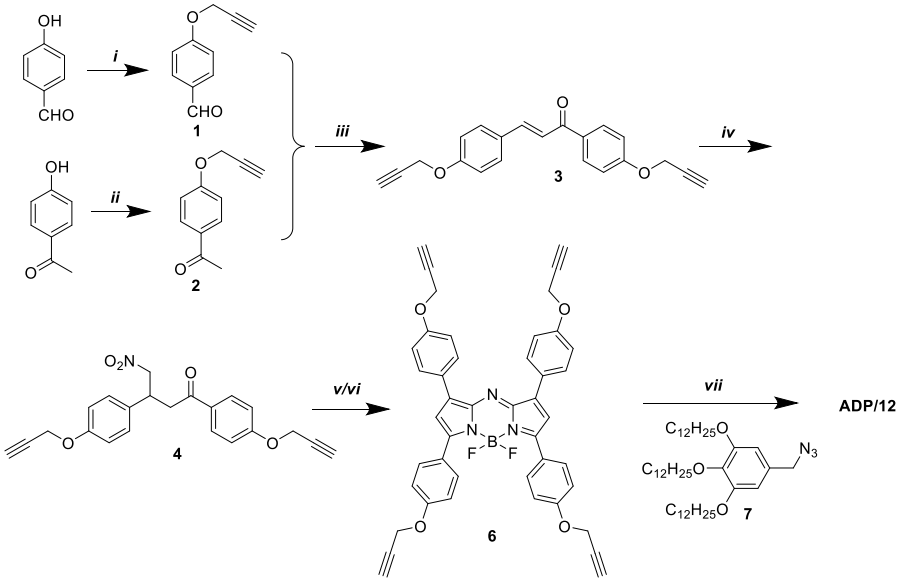


Fig. S9. Emission spectrum of the gel of **6-CN** (1×10^{-5} M) + **2ET/12** (1×10^{-5} M), the insert is the photo of the **2ET/12**, **6-CN + 2ET/12**, **6-CN** solution in THF under 365 nm UV light. (b) CIE coordinates of **6-CN + 2ET/12**.

2 Materials synthesis and analytical data



Scheme S1 Synthesis of compounds **ADP/12**: *Reagents and conditions*: (*i*) 3-Bromopropyne, acetone, K_2CO_3, 90 °C, 8 h, 93%; (*ii*) 3-Bromopropyne, acetone, K_2CO_3, 90 °C, 8 h, 94%; (*iii*) C_2H_5OH, KOH, H_2O, RT, 6 h, 89%; (*iv*) CH_3NO_2, $(C_2H_5)_2NH$, CH_3OH, reflux, 12 h, 76%; (*v*) NH_4OAc, C_2H_5OH, 80 °C, 48 h; (*vi*) $BF_3 \cdot Et_2O$, DIPEA, CH_2Cl_2, RT, 10 h, 31%; (*vii*) tert-Butanol, THF, H_2O, sodium ascorbate, $CuSO_4 \cdot 5H_2O$, RT, 12 h, 75%.

General Remarks

Commercially available chemicals were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-400 spectrometer and Bruker–DRX-600 spectrometers. Elemental analysis was performed using an Elementar VARIO EL elemental Analyzer. Column chromatography was performed with Merck silica gel 60 (230 - 400 mesh).

General procedure for the synthesis of 3,4,5-tris(alkyl)benzyl azide 7

Compound **7** were synthesized according to literature procedures in ref.[S3]

4-propargyloxy benzaldehyde 1.

Into a 100 mL round-bottom flask were added 4-hydroxybenzaldehyde (20 mmol, 2.44 g), propargyl bromide (20 mmol, 1.49 ml), K_2CO_3 (20 mmol, 2.76 g) and acetone (30 mL). The reaction mixture was refluxed for 8 h. the mixture was extracted twice with dichloromethane and the combined organic layers were dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography (eluent: petroleum ether : EtOAc : = 5 : 1) to give yellow oily compound **1**. Yield: 93%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.86 (s, 1H, ArCO**H**), δ = 7.83-7.81 (d, 2H, J = 8.4 Hz, 2 Ar**H**), δ = 7.07-7.05 (d, 2H, J = 8.4 Hz, 2 Ar**H**), δ = 4.75 (s, 2H, ArOC**H**$_2$), δ = 2.57 (s, 1H, alkyne-**H**).

4-propargyloxy acetophenone 2

Into a 100 mL round-bottom flask were added 4-hydroxybenzaldehyde (20 mmol, 2.72 g), propargyl bromide (20 mmol, 1.49 ml), K_2CO_3 (20 mmol, 2.76 g) and acetone (30 mL). The mixture was stirred for about 8 h. Upon completion, EtOAc and H_2O were added, the aqueous layer was extracted with EtOAc, and the combined organic layers were dried over $MgSO_4$, and concentrated by rotary evaporation. The residue was purified by column chromatography (eluent: petroleum ether : EtOAc : = 4 : 1) to give compound **2**. White solid, yield: 94 %, ^{1} H NMR (400 MHz, CDCl3) δ = 7.99-7.97 (d, 2H, J = 9.0 Hz, 2 Ar**H**), δ = 7.05-7.03 (d, 2H, J = 9.0 Hz, 2 Ar**H**), δ = 4.78-4.77 (d, 2H, J = 2.4 Hz, ArOC**H**$_2$), δ = 2.54-2.53 (m, 4H, -C**H**$_3$ and alkyne-**H**).

1,3-Di[4-(2-Propynyloxy) phenyl]propanone 3

A solution of compound **2** (10 mmol, 1.74 g) in ethanol (10 mL) was added gradually to an aqueous solution of 10% KOH (30 mL) at 0ºC. After stirring for 15 min, compound **1** (1.60 g, 10 mmol) was added and stirred at 0ºC for 15 min. The mixture was then allowed to attain room temperature and stirred for 6 h. After the reaction was completed, the precipitate was filtered, washed with cold ethanol and water, and dried under vacuum to afford a white solid. Yield: 89 % ^{1}H NMR (400 MHz, CDCl3): δ = 8.05-8.03 (d, 2H, J = 8.8 Hz, 2 Ar**H**), δ = 7.80-7.76 (d, 1H, J = 15.6 Hz, ArC**H**), δ = 7.63-7.61 (d, 2H, J = 8.4 Hz, 2 Ar**H**), δ = 7.46-7.42 (d, 1H, J = 15.6 Hz, ArCHC**H**), δ = 7.08-7.05 (d, 2H, J = 8.8 Hz, 2Ar**H**), δ = 7.03-7.01 (d, 2H, J = 8.4 Hz, 2Ar**H**), δ = 4.78 (d, 2H, J = 2.4 Hz, ArOC**H**$_2$), δ = 4.75-4.74 (d, 2H J = 2.0 Hz, ArOC**H**$_2$), δ = 2.57-2.56 (m, 2H, 2 alkyne-**H**).

3-[4-(2-Propynyloxy)phenyl]-4-nitro-1-[4-(2-propynyloxy)phenyl]-butan-1-one 4

To the solution of compound **3** (1.17 g, 3.6 mmol) in methanol (30 ml) was added diethylamine (1.8 mL, 18 mmol,) and nitromethane (18 mmol, 1.2 mL). The mixture was then heated under reflux for 24 h. The solution was cooled and evaporated to dryness under vacuum. The residue was purified by silica gel chromatography with CH_2Cl_2/petrol ether (1:1) as eluant to afford a yellow powder. Yield: 76%. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.91-7.90 (d, 2H, J = 6.6 Hz, 2 Ar**H**), δ = 7.21-7.20 (d, 2H, J = 6.6 Hz, 2 Ar**H**), δ = 7.01-7.00 (d, 2H, J = 7.2 Hz, 2 Ar**H**), δ = 6.93-6.92 (d, 2H, J = 6.6 Hz, 2 Ar**H**), δ = 4.81-4.78 (m, 1H, NO_2C**H**$_2$), δ = 4.75 (d, 2H, J = 1.8 Hz,

ArOC**H**$_2$), δ = 4.65 (d, 2H, J = 1.8 Hz, ArOC**H**$_2$), δ = 4.64-4.62 (m,1H NO_2C**H**$_2$), δ = 4.18-4,15 (t, 1H, J = 7.2 Hz, ArC**H**CH_2), δ = 3.40-3.32 (m, 2H, ArCHC**H**$_2$), δ = 2.55 (s, 1H, alkyne-**H**).), δ = 2.51 (s, 1H, alkyne-**H**).

BF_2 chelate of {3,5-di[4-(2-propynyloxy)phenyl]-1H-pyrrol-2-yl} {3,5-di[4-(2-propynyloxy)-phenyl]pyrrol-2-ylidene}amine 6

A mixture of **4** (1.5g, 3.97 mmol) and ammonium acetate (13.78g, 0.178 mol) in ethanol (30 mL) was stirred under reflux for 48 h. After cooling, the mixture was concentrated under reduced pressure Then CH_2Cl_2 (200 mL) and water (50 mL) were added. The organic layer was separated, washed with water (3 × 50 mL) and dried over $MgSO_4$. The solvent was evaporated to give the product as a dark blue solid **5** which was used in the next step. The crude product was dissolved in dry CH_2Cl_2 (30 mL), treated with diisopropylethylamine (0.7 mL, 4.0 mmol) and boron trifluoride diethyl etherate (1 mL, 8.13 mmol), and stirred at room temperature under N_2 for 10 h. The mixture was washed with water (50 mL), and organic layer was dried over $MgSO_4$ and evaporated to dryness. Purification by column chromatography on silica eluting with CH_2Cl_2/petrol ether (1:1) and evaporation of the solvent gave the brown solid. Yield: 31%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.08-8.03 (m, 8H, 8 Ar**H**), δ = 7.10-7.06 (m, 8H, 8 Ar**H**), δ = 6.95 (s, 2H, pyrrole-**H**), δ = 4.79-4,76 (m, 8H, 4 ArOC**H**$_2$), δ = 2.60(s, 2H, 2 alkyne-**H**), δ = 2.57 (s, 2H, 2 alkyne-**H**).

^{13}C NMR ([D_6]DMSO, 100 MHz): 160.1, 159.0, 157.6, 144.9, 142.3, 131.9, 131.1, 125.6, 124.5 118.9, 115.7, 115.6, 79.5, 79.3, 79.2, 79.0, 56.2, 56.1.

The procedure for the synthesis of the compounds **ADP/12**.

Compound **6** (412 mg, 0.6 mmol), compound **7** (72 mg, 0.1 mmol) were dissolved in THF (15 mL), tert-butyl alcohol : H_2O = 1 : 1 (2 mL), $CuSO_4 \cdot 5H_2O$ (120 mg, 0.48 mmol) and sodium ascorbate (158 mg, 0.8 mmol) were added. The mixture was stirred 20 h at RT. The solvent was removed in vacuo. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine, dried over MgSO4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (eluent : CH_2Cl_2 : petrol ether = 2 : 1). Dark blue solid, yield: 75%.

ADP/12: ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): δ = 8.03-7.94 (br, 8 H, 8 Ar**H**), δ = 7.59 (s, 4 H, 4 triazole-**H**), δ = 7.06-7.00 (br, 8 H, 8 ArH), δ = 6.91 (s, 2H, pyrrole-**H**), δ = 6.47 (s, 8 H, 8 Ar**H** and 2 pyrrole-**H**), δ = 5.40 (s, 8 H, 4 ArOC**H**$_2$-triazole), δ = 5.28 (s, 8 H, 4 triazole-C**H**$_2$Ar), δ = 3.93-3.91 (t, 24 H, J = 6.0 Hz, 12 ArOC**H**$_2$), δ = 1.76-1.73 (m, 24 H, 12 $ArOCH_2$C**H**$_2$), δ = 1.44 (s, 24 H, 12 $ArOCH_2CH_2$C**H**$_2$), δ = 1.28 (s, 192 H, 96 C**H**$_2$), δ = 0.88-0.86 (t, 36 H, J = 5.4 Hz, 12 C**H**$_3$).

^{13}C NMR ($CDCl_3$, 100 MHz): 153.6, 150.0, 138.6, 129.2, 122.9, 115.5, 115.0, 114.6, 106.8, 73.5, 69.3, 54.6, 31.9, 31.8, 30.3, 29.7, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1 (multi carbons in alkyl chain). Elemental analysis calcd (%) for $C_{216}H_{346}BF_2N_{15}O_{16}$ (3458.04); C, 75.02; H, 10.09; N, 6.08; Found: C, 74.32; H, 9.85; N, 5.56

3 ^{1}H and ^{13}C NMR spectra for representative compounds

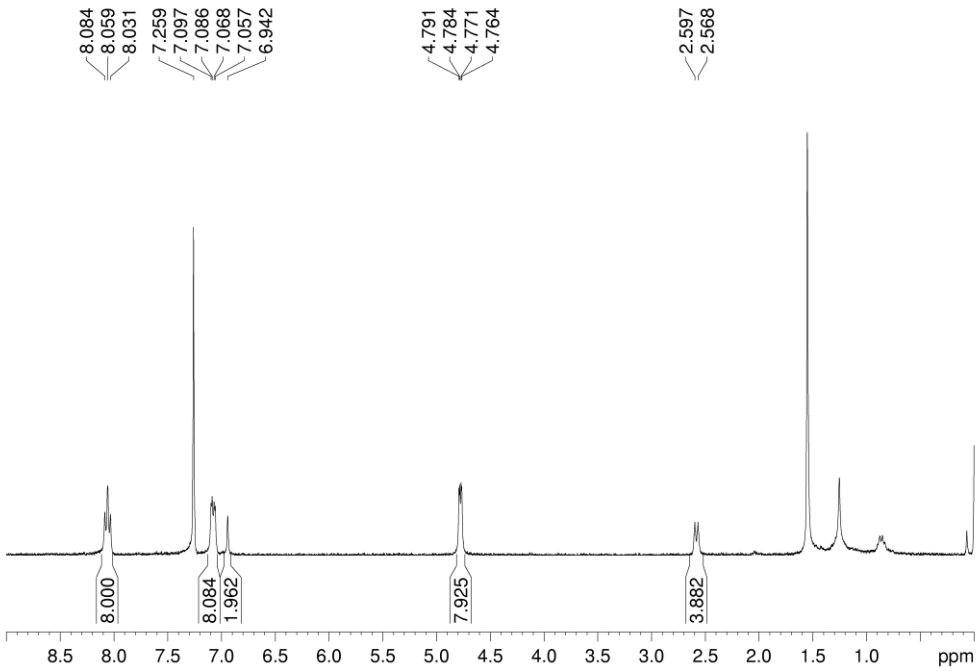


Fig. S10. ^{1}H NMR ($CDCl_3$, 400 MHz ppm) spectra of compound **6**.

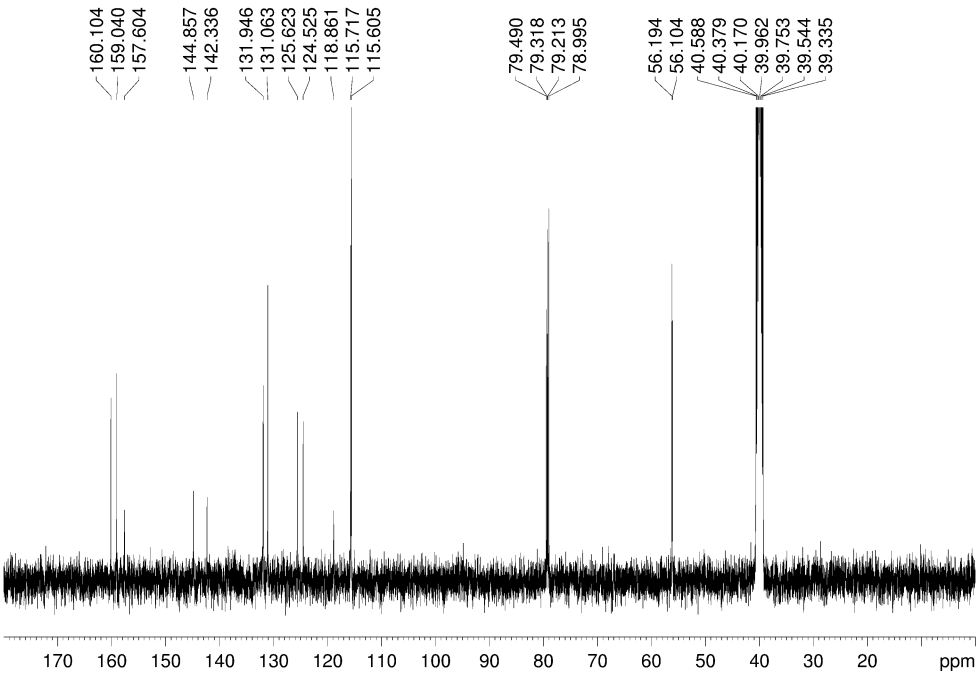


Fig. S11. ^{13}C NMR ($[D_6]$DMSO, 100 MHz) spectra of compound **6**

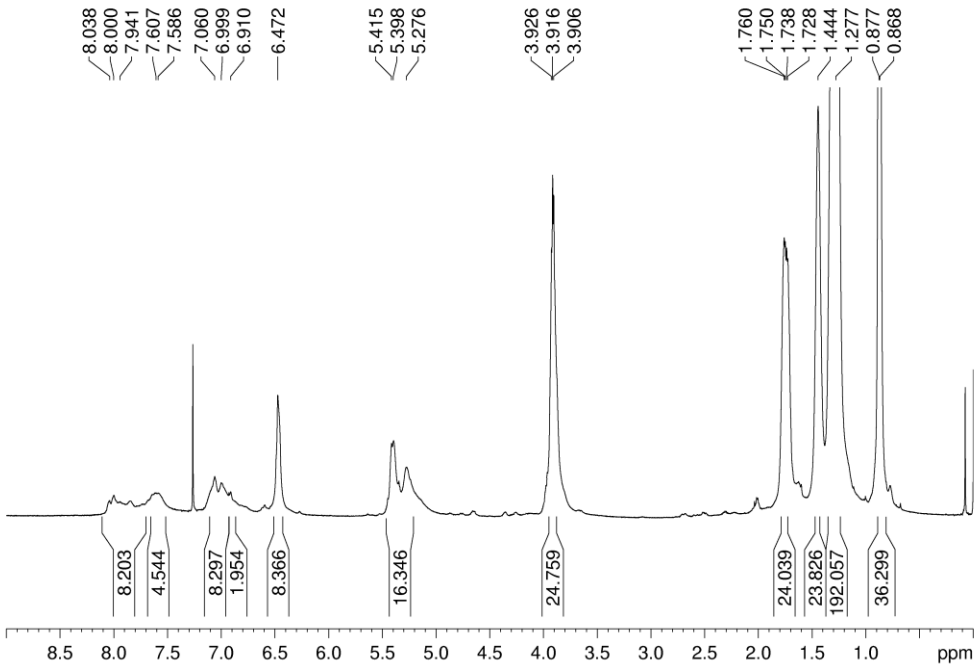


Fig. S12. ^{1}H NMR ($CDCl_3$, 600 MHz ppm) spectra of compound **ADP/12**.

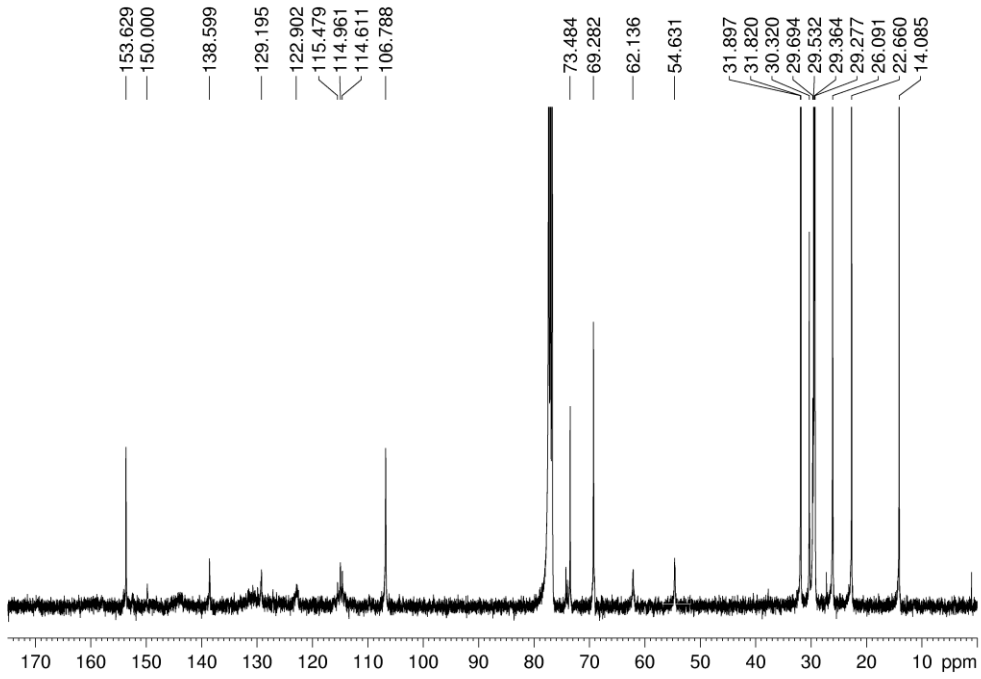


Fig. S13. ^{13}C NMR ($CDCl_3$, 100 MHz ppm) spectra of compound **ADP/12**.

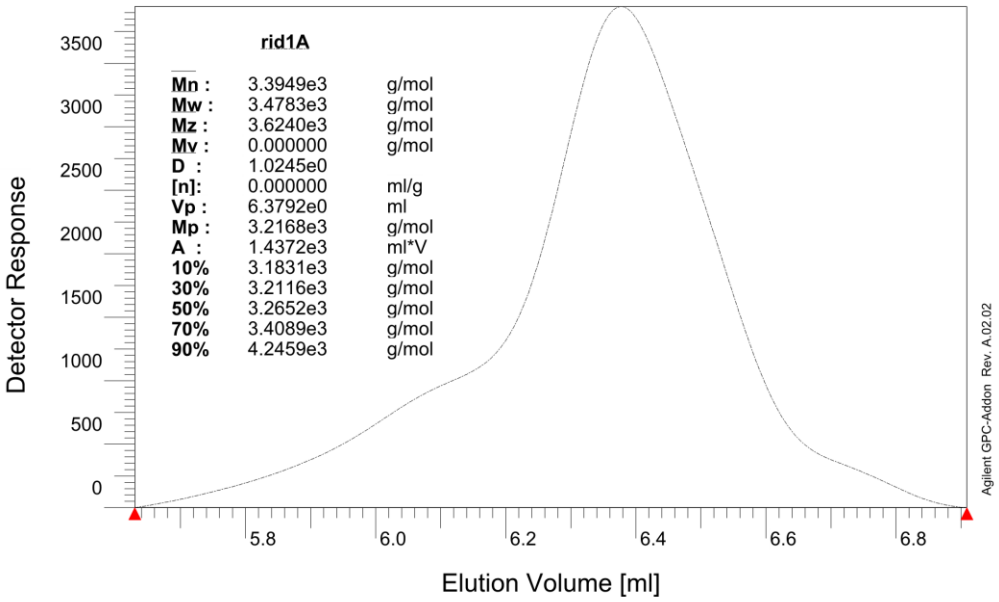


Fig. S14. The Gel Permeation Chromatography (GPC) of **ADP/12**.

S1 A. Immirzi, and B. Perini, *Acta Cryst. Sect. A*, 1997, **33**, 216 - 218.

S2 A. I. Kitaigorodsky, Molekülkristalle, and Akademieverlag Berlin, 1979.

S3 (a) X. P. Tan, L. Y. Kong, H. Dai, X. H. Cheng, F. Liu and C. Tschierske, *Chem. Eur. J.*, 2013, **19**, 16303 - 16313; (b) M. Lammens, J. Skey, S. Wallyn, R. O'Reilly and F. D. Prez, *Chem. Commun.*, 2010, **46**, 8719 - 8721; (c) D. X. Huang, M. Prehm, H. F. Gao, X. H. Cheng, Y. S. Liu and C. Tschierske, *RSC Adv.*, 2016, **6**, 21387 -21395.