Supporting Information

Synthesis and self-assembly of bent core polycatenar mesogens with binding selectivity to Hg^{2+}

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Content

1 Additional experimental data

1.1 Experimental techniques

A Mettler heating stage (FP 82 HT) was used for polarizing optical microscopy (POM, Optiphot 2, Nikon) and DSC traces were recorded with a DSC 200 F3 Maia calorimeter (NETZSCH) at 2 K min^{-1}. Fluorescence spectra were recorded using a Hitachi F-7000 fluorescence spectrometer (Hitachi, Japan). SEM experiments were carried out on a QUNT200 scanning electron microscopy (SEM, USA). All pictures were taken digitally. For the sample preparation, the gel was placed on a aluminum foil paper for some time until the gel become dry gel, then the sample was gold plated, finally the sample was put the sample into the scanning electron microscopy for observation.

Small-angle X-ray scattering (SAXS) experiments were performed in transmission mode with synchrotron radiation at the 1W2A SAXS beamline at Beijing Accelerator Laboratory and beamline BL16B1 Shanghai Synchrotron Radiation Facility. A modified Linkam hot stage with a thermal stability within 0.2 °C was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. Samples were held in the poly(imide) (Kapton) film. A MarCCD 165 detector was used. *q* calibration and linearization were verified using several orders of layer reflections from silver behemate. Positions and intensities of the diffraction peaks were measured using PeakSolve™ (Galactic).

1.2 Additional textures of LC phases and DSC traces

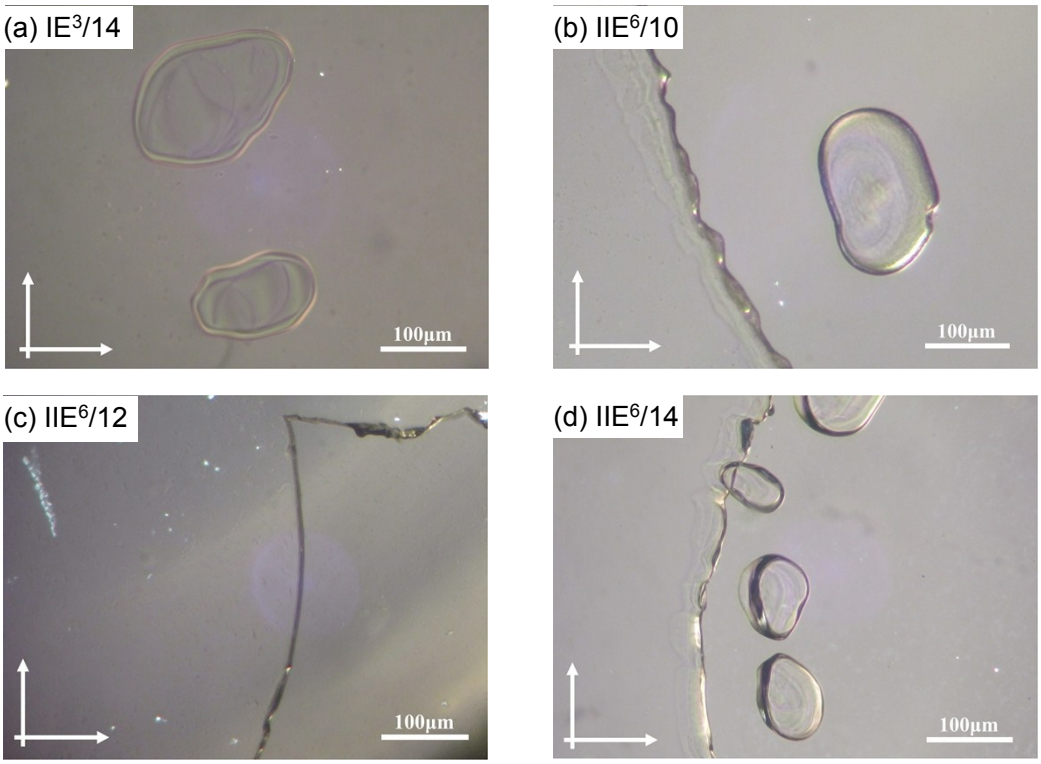
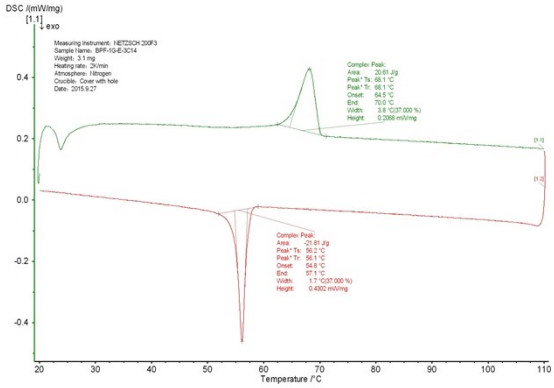
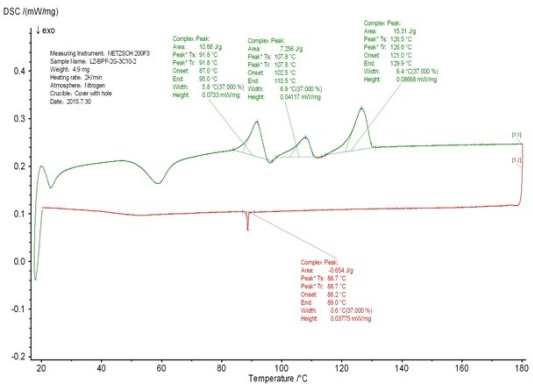


Figure S1. Textures of the $Cub_I / Pm\bar{3}n$ phases as observed under POM for compounds **IIE^{m}/n**: a) **IE^{3}/14** at T = 65 °C; **b) IIE^{6}/10** at T =65 °C; c) **IIE^{6}/12** at T =77 °C; d) **IIE^{6}/14** at T = 70 °C.

(a) IE^{3}/14



(b) IIE^{6}/10



(c) IIE^{6}/12

(d) IIE^{6}/14

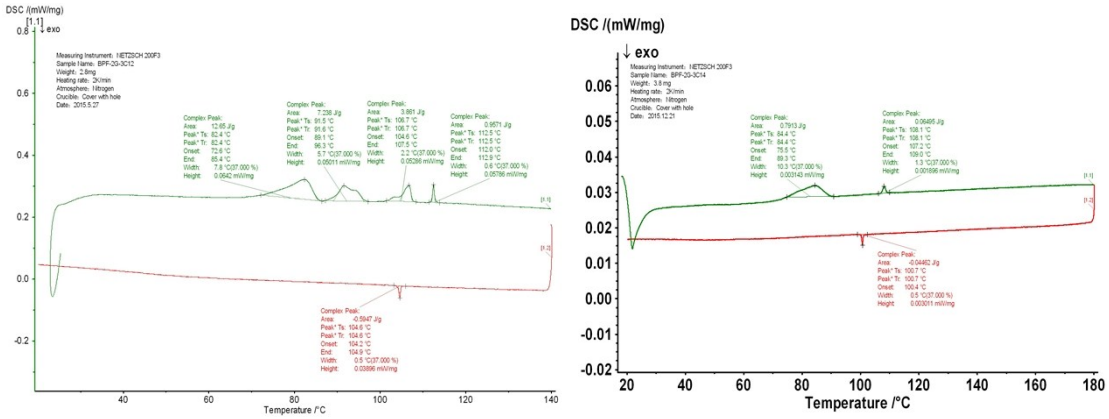


Figure S2. DSC heating and cooling scans (2 K min^{-1}) of (a) compound **IE^3/14** (second scans); (b) compound **IIE^6/10** (second scans); (c) compound **IIE^6/12** (first scans); (d) compound **IIE^6/14** (first scans).

1.3 Additional XRD data

Table S1 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	Unit cell parameters /nm(T/°C)	micelle size D/nm	V_{cell}/nm^3	V_{mol}/nm^3	$n_{cell,cryst}$	$n_{cell,liq}$	n_{cell} (average)
IE^3/14	$Pm\bar{3}n$	11.09(75)	5.55(75)	1364	3.06	445.8	350.3	398.1
IIE^6/10	$Pm\bar{3}n$	9.05(95)	4.53(95)	741.2	4.70	157.7	123.9	140.8
IIE^6/12	$Pm\bar{3}n$	9.46(90)	4.73(90)	846.6	5.29	160.0	125.7	142.8
IIE^6/14	$Pm\bar{3}n$	9.32(100)	4.66(100)	809.5	5.89	137.4	107.9	122.7

[a] $D = 0.5\times a_{cub}$ for $Pm\bar{3}n$; V_{cell} = volume of the unit cell defined by the dimensions a_{cub}^3 for the cubic 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 S2. Comparison of n_{cell}(average) and $n_{cell}(\rho)$ values for compounds **IE^3/14** and **IIE^m/n**.[a]

Comp.	T/°C	n_{cell}(average)	$n_{cell}(\rho)$
IE^3/14	75	392.8	393.9
IIE^6/10	95	140.8	141.2
IIE^6/12	90	142.8	143.3
IIE^6/14	100	122.7	123.4

[a] The number of molecules in a 3D unit cell was calculated from the volume of this unit cell (V_{cell}) and the volume of a molecule (V_{mol}, calculated using crystal volume increments[S1]) according to $n_{cell} = V_{cell}/V_{mol}$. $V_{cell} = a_{cub}^3$ was as collated in Table S1. The values n_{cell}(average)

were obtained as the average of the $n_{cell,cryst}$ and $n_{cell,liq}$. In order to verify the feasibility of these values, we measured the density of compounds **IE^3/14** and **IIE^m/*n*** with the floating equilibrium method at room temperature (**IE^3/14:** ρ = 0.960 g cm^{-3}; **IIE^6/10:** ρ = 1.002 g cm^{-3}; **IIE^6/12:** ρ = 0.985 g cm^{-3}; **IIE^6/14:** ρ =0.972 g cm^{-3}). The values $n_{cell}(\rho)$ were obtained according to the formula $n_{cell}(\rho) = a^3\rho N_A/M$ (M = molecular mass, N_A = the Avagadro constant, ρ = the density). We find that the values n_{cell} obtained from average packing coefficient and $n_{cell}(\rho)$ obtained from the measured density are very close. This indicates that the obtained values n_{cell}(average) are reliable, especially considering that the density at higher temperature should be a bit lower and in this way $n_{cell}(\rho)$ becomes smaller and approaches even closer to n_{cell}(average).

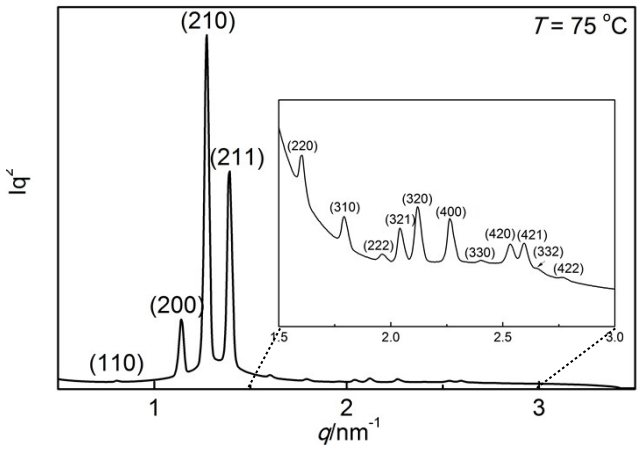


Figure S3. SAXS diffractogram (synchrotron source) of the Cub$_I$ / $Pm\bar{3}n$ phase of compound **IE^3/14** at T = 75 °C.

Table S3 Experimental and calculated *d*-spacing of the observed SAXS reflection of the cubic phase in **IE^3/14** at T = 75 ºC. All intensity values are Lorentz and multiplicity corrected.[a]

(*hkl*)	$d_{obs.}$– spacing(nm)	$d_{cal.}$– spacing(nm)	*intensity*	*lattice paremeter*(nm)
(110)	7.80	7.81	0.31	a_{110} = 11.03
(200)	5.51	5.52	15.96	a_{200} = 11.02
(210)	4.94	4.94	100	a_{210} = 11.05
(211)	4.51	4.51	59.35	a_{211} = 11.05
(220)	3.92	3.90	0.52	a_{220} = 11.09
(310)	3.51	3.49	0.56	a_{310} = 11.10
(222)	3.20	3.19	0.13	a_{222} = 11.09
(320)	3.08	3.06	0.64	a_{320} = 11.11
(321)	2.97	2.95	1.18	a_{321} = 11.11
(400)	2.78	2.76	0.99	a_{400} = 11.12
(330)	2.62	2.60	0.05	a_{330} = 11.12
(420)	2.48	2.47	0.35	a_{420} = 11.09
(421)	2.42	2.41	0.35	a_{421} = 11.09
(332)	2.38	2.35	0.02	a_{332} = 11.16

(422)	2.27	2.25	0.02	a_{422} = 11.12
a_{Cub} = 11.09 nm				

[a] $d_{hkl} = 2\pi/q_{hkl}$; $a_{hkl} = (h^2 + k^2 + l^2)^{1/2}\, d_{hkl}$; $a_{cub} = (a_{110} + a_{200} + a_{210} + a_{211} + a_{220} + a_{310} + a_{222} + a_{320} + a_{321} + a_{400} + a_{330} + a_{420} + a_{421} + a_{332} + a_{422})/15$.

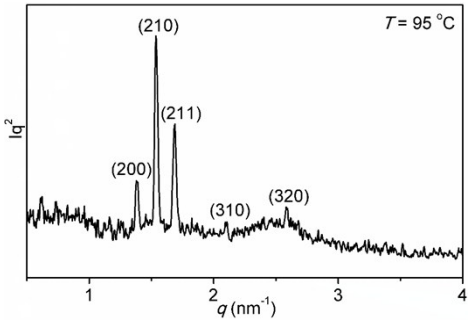


Figure S4. SAXS diffractogram (synchrotron source) of the Cub_I / $Pm\bar{3}n$ phase of compound **IIE^6/10** at T = 95 °C.

Table S4 Experimental and calculated *d*-spacing of the observed SAXS reflection of the cubic Cub_I/ $Pm\bar{3}n$ phase in **IIE^6/10** at T = 95 ºC. All intensity values are Lorentz and multiplicity corrected.[a]

(*hkl*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*lattice paremeter*(nm)
(200)	4.51	4.53	29.52	a_{200} = 9.02
(210)	4.05	4.05	100	a_{210} = 9.06
(211)	3.71	3.69	57.14	a_{211} = 9.09
(310)	2.85	2.87	9.05	a_{310} = 9.01
(320)	2.54	2.52	15.71	a_{320} = 9.10
a_{Cub} = 9.05 nm				

[a] $d_{hkl} = 2\pi/q_{hkl}$; $a_{hkl} = (h^2 + k^2 + l^2)^{1/2}\, d_{hkl}$; $a_{cub} = (a_{200} + a_{210} + a_{211} + a_{310} + a_{320})/5$.

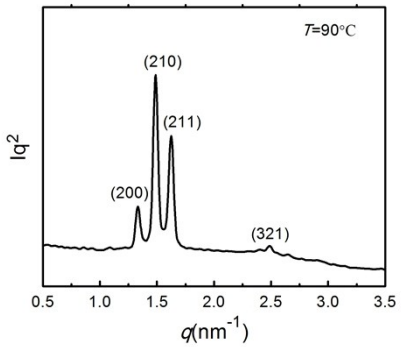


Figure S5. SAXS diffractogram (synchrotron source) of the Cub_I / $Pm\bar{3}n$ phase of compound **IIE^6/12** at T = 90 °C.

Table S5 Experimental and calculated *d*-spacing of the observed SAXS reflection of the cubic Cub_I / $Pm\bar{3}n$ phase in **IIE^6/12** at T = 90 ºC. All intensity values are Lorentz and multiplicity corrected.[a]

(*hkl*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*lattice paremeter*(nm)

(200)	4.72	4.72	23.49	$a_{200} = 9.44$
(210)	4.21	4.23	100	$a_{210} = 9.41$
(211)	3.88	3.86	63.76	$a_{211} = 9.50$
(321)	2.53	2.53	2.58	$a_{321} = 9.47$
$a_{Cub} = 9.46$ nm				

[a] $d_{hkl} = 2\pi/q_{hkl}$; $a_{hkl} = (h^2 + k^2 + l^2)^{1/2}\, d_{hkl}$; $a_{cub} = (a_{200} + a_{210} + a_{211} + a_{321})/4$.

Table S6 Experimental and calculated *d*-spacing of the observed SAXS reflection of the cubic Cub_I / $Pm\bar{3}n$ phase in **IIE⁶/14** at 100 ºC. All intensity values are Lorentz and multiplicity corrected.[a]

(*hkl*)	$d_{obs.}$ – spacing (nm)	$d_{cal.}$ – spacing (nm)	*intensity*	*lattice paremeter*(nm)
(110)	6.57	6.59	42.63	$a_{110} = 9.29$
(200)	4.65	4.66	13.24	$a_{200} = 9.30$
(210)	4.17	4.17	100	$a_{210} = 9.32$
(211)	3.81	3.80	65.99	$a_{211} = 9.33$
(220)	3.30	3.30	0.66	$a_{220} = 9.33$
(310)	2.96	2.95	49.8	$a_{310} = 9.36$
(222)	2.70	2.69	0.34	$a_{222} = 9.35$
(320)	2.59	2.58	1.31	$a_{320} = 9.34$
(321)	2.50	2.49	2.72	$a_{321} = 9.35$
(400)	2.34	2.33	0.66	$a_{400} = 9.32$
(420)	2.09	2.08	0.19	$a_{420} = 9.35$
(421)	2.04	2.03	0.24	$a_{421} = 9.32$
$a_{Cub} = 9.32$ nm				

[a] $d_{hkl} = 2\pi/q_{hkl}$; $a_{hkl} = (h^2 + k^2 + l^2)^{1/2}\, d_{hkl}$; $a_{cub} = (a_{110} + a_{200} + a_{210} + a_{211} + a_{220} + a_{310} + a_{222} + a_{320} + a_{321} + a_{400} + a_{420} + a_{421})/12$.

1.4 Gel properties

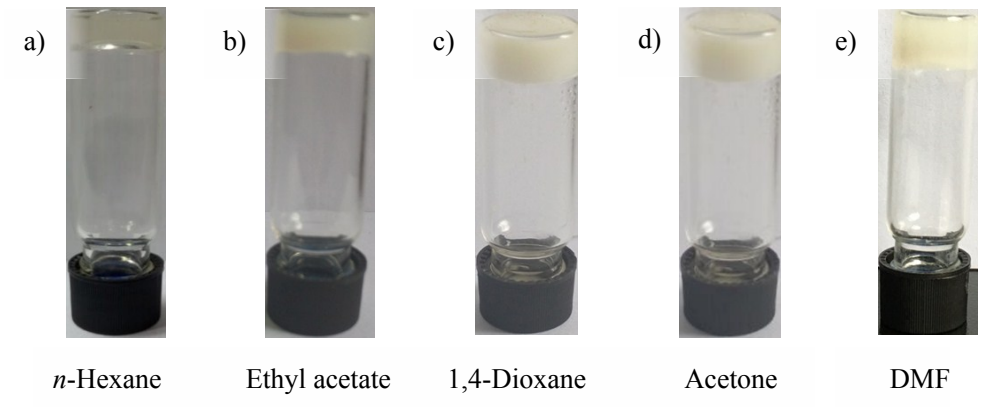


Figure S6. Gels of $IE^3/14$ (a) in *n*-Hexane; (b) in Ethyl acetate; (c) in 1,4-Dioxane; (d) in Acetone; (e) in DMF.

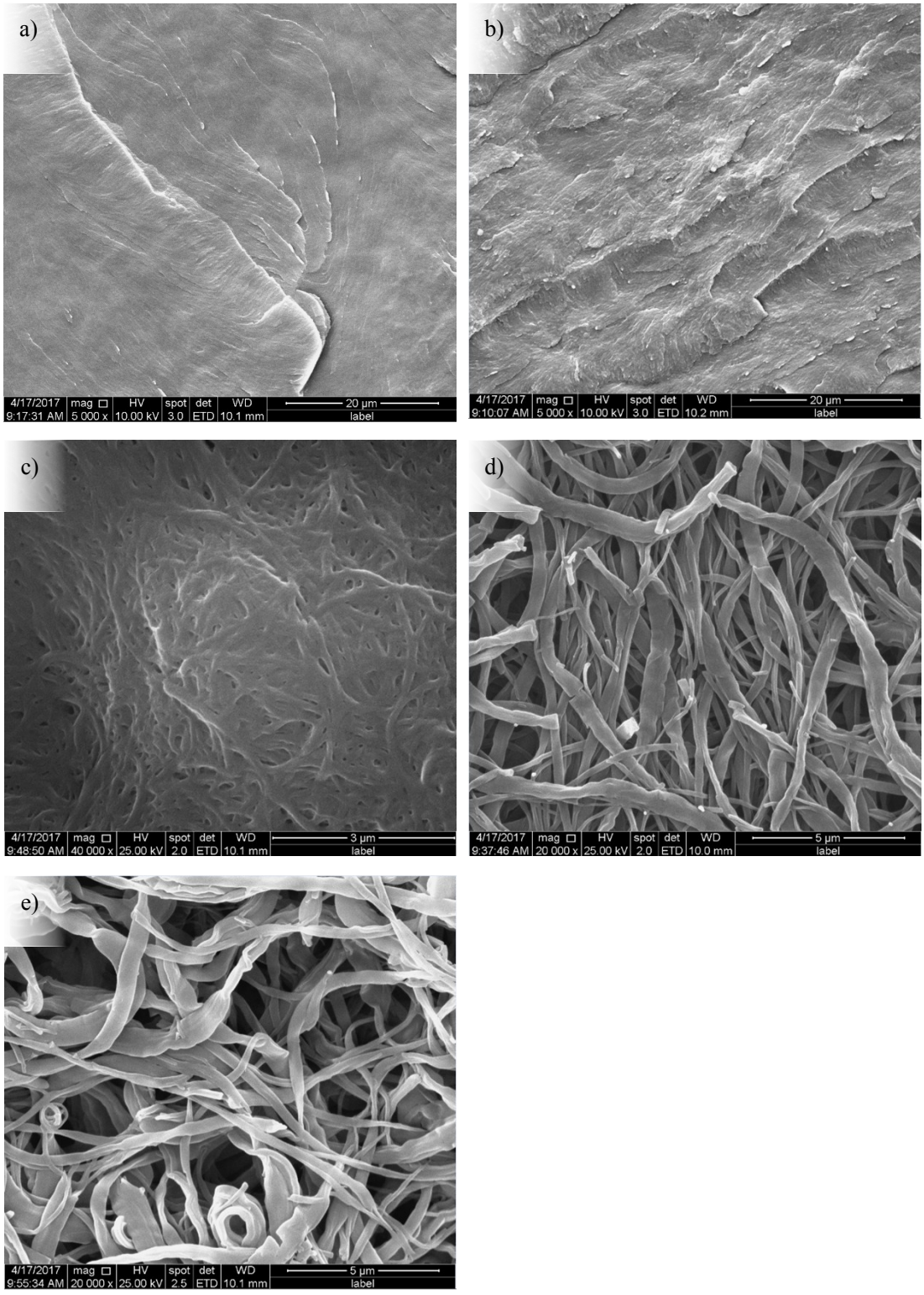


Figure S7. Selected SEM images of the dry gel made from **IE^3/14** (a) in *n*-Hexane, scale bar is 20 µm; (b) in Ethyl acetate, scale bar is 20 µm; (c) in 1,4-Dioxane, scale bar is 3 µm; (d) in Acetone, scale bar is 5 µm; (e) in DMF, scale bar is 5 µm.

1.5 Chemosensor behaviour

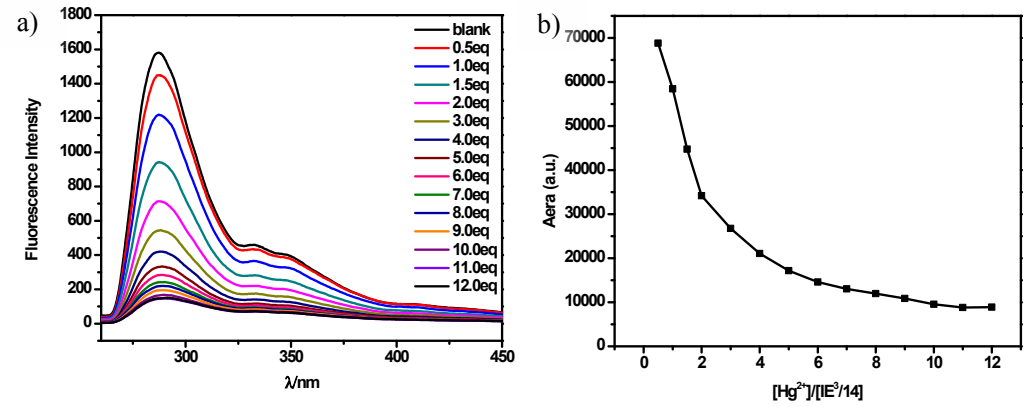


Figure S8. (a, b) Fluorescence spectra of compound **IE^3/14** (6.4×10^{-6} M) at 20 °C upon addition of Hg^{2+} (from 0.5 to 12.0 equiv) in CH_2Cl_2 : CH_3CN = 1 : 1 mixture (λ_{ex} = 240 nm).

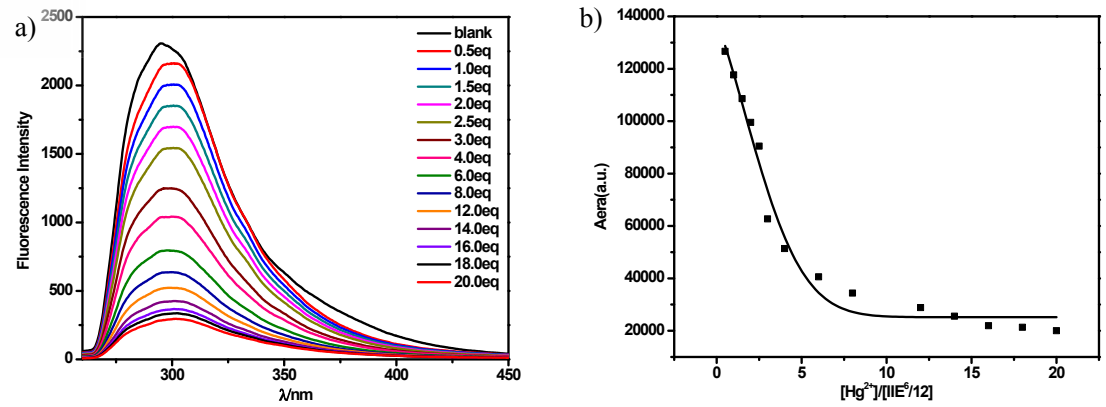


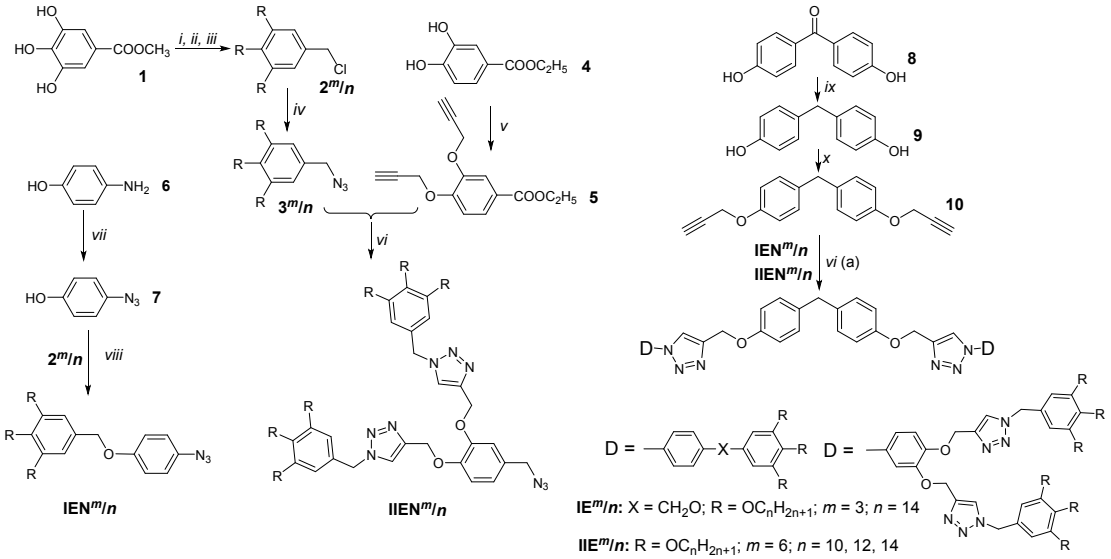
Figure S9. (a, b) Fluorescence spectra of compound **IIE^6/12** (5.0×10^{-6} M) at 20 °C upon addition of Hg^{2+} (from 0.5 to 12.0 equiv) in CH_2Cl_2 : CH_3CN = 1 : 1 mixture (λ_{ex} = 240 nm).

2 Synthesis and analytical data

2.1 General remarks

All reagents, unless otherwise specified, were obtained from Energy Chemical Company and used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker–DRX-400 spectrometer and Bruker–DRX-500 spectrometer. Column chromatography was performed with merck silica gel 60 (230-400 mesh). The intermediates were purified by column chromatography, their structures were confirmed by ^{1}H NMR and the purity was checked by TLC. Full analytic characterization was provided for all final compounds. The alkoxybenzyl chlorides **2*^{m}*/*n*** were prepared according to literature procedures.[S3,S4] The analytical data

correspond to those reported in the references.



Scheme 1. Synthesis of compounds **IE^{m}/*n*** and **IIE^{m}/*n***: *Reagents and conditions*: i) $C_nH_{2n+1}Br$, DMF, K_2CO_3, 90 °C; ii) $LiAlH_4$, THF, 25 °C, 2 h; iii) $SOCl_2$, THF, 25 °C, 1 h; *iv*) KI, NaN_3, DMF, 45 °C, 12 h; v) K_2CO_3, propargyl bromide, acetone, reflux; vi) a) tert-butanol, THF, H_2O, sodium ascorbate, $CuSO_4{\cdot}5H_2O$, 25 °C, 20 h; b) $LiAlH_4$, THF, 25 °C, 2 h; c) $SOCl_2$, THF, 25 °C, 1 h; d) KI, NaN_3, DMF, 45 °C, 12 h; vii) a) $NaNO_2$/HCl, 0 °C, 1 h; b) NaN_3, 0~5 °C, 5 h; viii) THF, NaH, 70 °C, ix) $LiAlH_4$, $AlCl_3$, THF, 65 °C; x) KOH, propargyl bromide, acetone, reflux.

2.2 Synthesis of 4-Azidophenol 7[S5]

4-Aminophenol **6** (1.8 g, 16.5 mmol) was suspended in aqueous hydrochloric acid (2 M, 36 mL), the mixture was cooled to 0 °C, and a solution of $NaNO_2$ (1.37 g, 20 mmol） in water (3 mL) was added. The mixture was stirred for 1 h at 0 °C, then a solution of NaN_3 (1.64 g, 25 mmol) in water (3 mL) was added and stirred for 5 h at 0~5 °C. Water (50 mL) and CH_2Cl_2 (50 mL) were added, the organic layer was separated, the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layer was washed with brine (2 × 20 mL) and dried over anhydrous Na_2SO_4 and the solvent were evaporated *in vacuo.* The residue was purified by column chromatography (petroleum ether : ethyl acetate = 8 : 1). Yield 1.7 g, 76 %; brownish solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm): 6.91-6.89 (d, 2 H, J = 7.4 Hz, Ar**H**), 6.83-6.81 (d, 2 H, J = 7.4 Hz, Ar**H**), 5.12 (s, 1 H, ArO**H**).

2.3 General procedure for the synthesis of IEN^{m}/n

To a mixture of NaH (118 mg, 4.94 mmol), 4-azidophenol **7** (334 mg, 2.47 mmol) in dry THF (20 mL), the appropriate alkoxybenzyl chloride **3^{3}/14** (1.88 g, 2.47 mmol) was added. The mixture was heated to 70 °C and stirred for 30 h. After the reaction was completed (TLC), the mixture was cooled to 25 °C and extracted with ethyl acetate (3 × 30 mL). The combined extracts were washed with H_2O (5 × 20 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether/ethyl acetate = 5 : 1).

IEN^{3}/14: Yield: 1.27g, 60 %; light yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 6.95 (s, 4 H, Ar**H**), 6.60 (s, 2 H, Ar**H**), 4.92 (s, 2 H, ArC**H**$_2$O), 3.98-3.92 (m, 6 H, 3 ArOC**H**$_2$), 1.80-1.73 (m, 6 H, 3 ArOCH$_2$C**H**$_2$), 1.46-1.44 (m, 6 H, 3 ArOCH$_2$CH$_2$C**H**$_2$), 1.30-1.26 (m, 60 H , 30 C**H**$_2$), 0.89-0.86 (t, 9 H, J = 6.8 Hz ,3 C**H**$_3$).

2.4 General procedure for the synthesis of 3^{m}/n[S6]

The appropriate alkoxybenzyl chloride **2^{m}/n** (4.0 mmol) and NaN_3 (20.0 mmol) were dissolved in dry DMF (10 mL), KI (6.0 mmol) was added. The mixture was stirred over night at 45 °C. Afterwards, the solvent was removed *in vacuo*. Water (30 mL) and CH_2Cl_2 (90 mL) were added to the residue. The organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL) and washed with brine (3×20 mL), and dried over anhydrous Na_2SO_4, the solvent was removed in *vacuo*. The residue was purified by column chromatography (petroleum ether/ethyl acetate = 30:1).

3^{3}/10: Yield: 2.28 g, 95%, colourless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 6.49 (s, 2 H, Ar**H**), 4.24 (s, 2 H, ArC**H**$_2$N$_3$), 3.99-3.94 (m, 6 H, 3 ArOC**H**$_2$), 1.82-1.71

(m, 6 H, 3 $ArOCH_2C\mathbf{H}_2$), 1.48-1.43 (m, 6 H, 3 $ArOCH_2CH_2C\mathbf{H}_2$), 1.35-1.25 (m, 36 H, 18 $C\mathbf{H}_2$), 0.90-0.87 (t, 9 H, J = 6.0 Hz, 3 $C\mathbf{H}_3$).

3^3/12: Yield: 2.58 g, 94%, colourless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 6.48 (s, 2 H, Ar**H**), 4.24 (s, 2 H, $ArC\mathbf{H}_2N_3$), 3.99-3.93 (m, 6 H, 3 $ArOC\mathbf{H}_2$), 1.83-1.71 (m, 6 H, 3 $ArOCH_2C\mathbf{H}_2$), 1.47-1.43 (m, 6 H, 3 $ArOCH_2CH_2C\mathbf{H}_2$), 1.35-1.26 (m, 48 H, 24 $C\mathbf{H}_2$), 0.90-0.86 (t, 9 H, J = 6.0 Hz, 3 $C\mathbf{H}_3$).

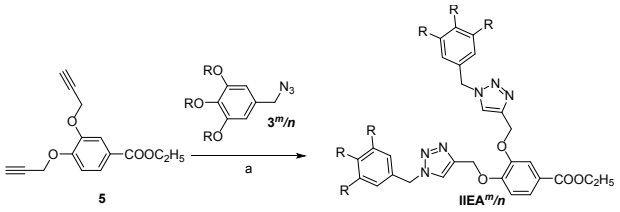
3^3/14: Yield: 2.96 g, 96%, colourless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 6.48 (s, 2 H, Ar**H**), 4.24 (s, 2 H, $ArC\mathbf{H}_2N_3$), 3.99-3.93 (m, 6 H, 3 $ArOC\mathbf{H}_2$), 1.83-1.72 (m, 6 H, 3 $ArOCH_2C\mathbf{H}_2$), 1.48-1.43 (m, 6 H, 3 $ArOCH_2CH_2C\mathbf{H}_2$), 1.35-1.26 (m, 60 H, 30 $C\mathbf{H}_2$), 0.90-0.86 (t, 9 H, J = 6.0 Hz, 3 $C\mathbf{H}_3$).

2.5 Synthesis of compound ethyl-3,4-dipropargyloxylbenzoate 5

Compound ethyl 3,4-dihydroxybenzoate **4** (2.0 mmol), propargyl bromide (6.0 mmol) and K_2CO_3 (8.0 mmol) were dissolved in dry acetone(10 mL) under a nitrogen atmosphere. The mixture was stirred over night at 50 °C. The solvent was removed in *vacuo*. The residue was extracted with ethyl acetate (2 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether/dichloromethane = 1 : 1). Yield: 454 mg, 88%, light yellow solid.

2.6 General procedure for the synthesis of IIEN^m/n

a) General procedure for the synthesis of IIEA^m/n



Compound **5** (1.2 mmol), Compound **IN^m/n** (2.5 mmol) was dissolved in THF (6 mL),

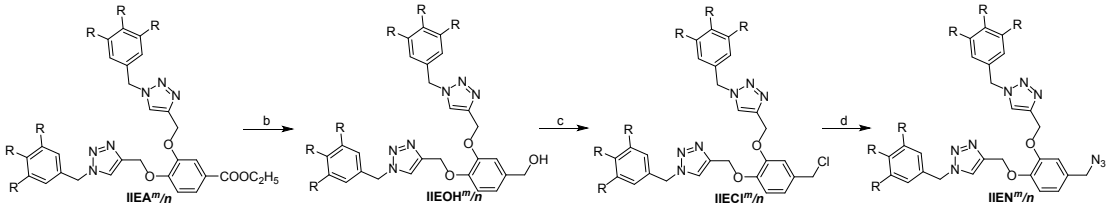
tert-Butyl alcohol : H_2O = 1 : 1 (2 mL)，$CuSO_4 \cdot 5H_2O$ (50 mg, 0.2 mmol) and sodium ascorbate (1.0 M in H_2O, 30 drops) were added. The mixture was stirred at 25 °C for 20 h. The solvent was removed in *vacuo*. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over $MgSO_4$, then the solvent was removed in *vacuo*. The residue was purified by chromatography (CH_2Cl_2: ethyl acetate = 40 : 1).

IIEA^3/10: Yield: 1.26 g, 72%; white crystal. ^{1}H NMR ($CDCl_3$, 400 MHz) , δ (ppm) : 7.70 (s, H ,Triazole-**H**), 7.67 (s, H ,Triazole-**H**), 7.64-7.61 (d, 2H, J = 10.0 Hz, Ar**H**), 7.08-7.06 (d, 1H, J = 8.4 Hz, Ar**H**), 6.48 (s, 4 H, Ar**H**), 5.40 (s, 4H, ArOC**H**$_2$-triazole), 5.28-5.25 (d, 4H, J = 10.8Hz, ArC**H**$_2$N$_3$), 4.36-4.34 (m, 2H, OC**H**$_2$CH$_3$), 3.94-3.90 (m, 12H, 6OC**H**$_2$CH$_2$CH$_2$), 1.80-1.72 (m, 12H, 6OCH$_2$C**H**$_2$CH$_2$), 1.47-1.28 (m, 87H, 42C**H**$_2$, OCH$_2$C**H**$_3$), 0.91-0.88 (t, 18H, J = 6.4 Hz, 6C**H**$_3$).

IIEA^3/12: Yield: 1.45 g, 74%; white crystal. ^{1}H NMR ($CDCl_3$, 400 MHz) , δ (ppm) : 7.70 (s, H ,Triazole-**H**), 7.67 (s, H ,Triazole-**H**), 7.64-7.61 (d, 2H, J = 10.0 Hz, Ar**H**), 7.08-7.06 (d, 1H, J = 8.4 Hz, Ar**H**), 6.48 (s, 4 H, Ar**H**), 5.40 (s, 4H, ArOC**H**$_2$-triazole), 5.28-5.25 (d, 4H, J = 10.8Hz, ArC**H**$_2$N$_3$), 4.36-4.34 (m, 2H, OC**H**$_2$CH$_3$), 3.94-3.90 (m, 12H, 6OC**H**$_2$CH$_2$CH$_2$), 1.80-1.72 (m, 12H, 6OCH$_2$C**H**$_2$CH$_2$), 1.47-1.28 (m, 111H, 54C**H**$_2$, OCH$_2$C**H**$_3$), 0.91-0.88 (t, 18H, J = 6.4 Hz, 6C**H**$_3$).

IIEA^3/14: Yield: 1.47 g, 68%; white crystal. ^{1}H NMR ($CDCl_3$, 400 MHz) , δ (ppm) : 7.70 (s, H ,Triazole-**H**), 7.67 (s, H ,Triazole-**H**), 7.64-7.61 (d, 2H, J = 10.0 Hz, Ar**H**), 7.08-7.06 (d, 1H, J = 8.4 Hz, Ar**H**), 6.48 (s, 4 H, Ar**H**), 5.40 (s, 4H, ArOC**H**$_2$-triazole), 5.28-5.25 (d, 4H, J = 10.8Hz, ArC**H**$_2$N$_3$), 4.36-4.34 (m, 2H, OC**H**$_2$CH$_3$), 3.94-3.90 (m, 12H, 6OC**H**$_2$CH$_2$CH$_2$), 1.80-1.72 (m, 12H, 6OCH$_2$C**H**$_2$CH$_2$), 1.47-1.28 (m, 135H, 66C**H**$_2$, OCH$_2$C**H**$_3$), 0.91-0.88 (t, 18H, J = 6.4 Hz, 6C**H**$_3$).

b) General procedure for the synthesis of IIEOH^m/*n*



Compound **IIEA^{m}/$_{n}$** (0.4 mmol) was dissolved in dry THF (6 mL), then slowly add the $LiAlH_4$ (0.6 mmol, 23 mg) and placed in an ice bath. The mixture was reacted 2 h at room temperature. Water was then added slowly with vigorous stirring to terminate the reaction, and then diluted HCl was added to dissolve the precipitate. The product was extracted with CH_2Cl_2. The extracts were dried over anhydrous $MgSO_4$, The solvent was removed in *vacuo*. The obtained product was directly used for the next reaction.

c) General procedure for the synthesis of IIECl^{m}/$_{n}$

The resulting benzyl alcohol **IIEOH^{m}/$_{n}$** was converted to benzyl chloride **IIECl^{m}/$_{n}$** with thionyl chloride ($SOCl_2$) in dry THF (6 mL) and then added the 2 drops of DMF as catalyst. The reaction was stirred at 25 °C for 1 h, at which point the reaction was complete by TLC in (CH_2Cl_2: ethyl acetate = 40 : 1). The solvent and excess of $SOCl_2$ were removed at reduced pressure, affording the pure product, which was used without further purification and directly into the next reaction.

d) General procedure for the synthesis of IIEN^{m}/$_{n}$

The appropriate **IIECl^{m}/$_{n}$** (0.4 mmol) and NaN_3 (2.0 mmol) were dissolved in dry DMF (10 mL), KI (0.6 mmol) was added. The mixture was stirred over night at 45 °C. Afterwards, water (30 mL) and CH_2Cl_2 (90 mL) were added to the residue. The organic layer was separated and washed with brine (5×20 mL), and dried over anhydrous Na_2SO_4, the solvent was removed *in vacuo*. The residue was purified by column chromatography (CH_2Cl_2: ethyl acetate = 40 : 1).

IIEN^{6}/10: Yield: 549 mg, 95%, colourless solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ

(ppm): 7.59-7.58 (d, 2 H, *J* = 4.4 Hz, triazole-**H**), 7.02-7.00 (d, 1 H, *J* = 8.4 Hz, Ar**H**), 6.98-6.97 (d, 1 H, *J* = 4.0 Hz, Ar**H**), 6.86-6.84 (dd, 1 H, *J* = 1.6 Hz, *J* = 2.0 Hz, Ar**H**), 6.46 (s, 4 H, Ar**H**), 5.37-5.36 (d, 4 H, *J* = 2.8 Hz, ArC**H**$_2$-triazole), 5.22-5.21 (d, 4 H, *J* = 6.8 Hz, ArOC**H**$_2$-triazole), 4.22 (s, 2 H, ArC**H**$_2$N$_3$), 3.93-3.87 (m, 12 H, 6 ArOC**H**$_2$), 1.79-1.70 (m, 12 H, 6 ArOCH$_2$C**H**$_2$), 1.45-1.40 (m, 12 H, 6 ArOCH$_2$CH$_2$C**H**$_2$), 1.35-1.24 (m, 72 H, 36 C**H**$_2$), 0.89-0.86 (t, 18 H, *J* = 6.8 Hz, 6 C**H**$_3$).

IIEN^6/12: Yield: 606 mg, 94%, colourless solid. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* (ppm): 7.59-7.58 (d, 2 H, *J* = 4.4 Hz, triazole-**H**), 7.02-7.00 (d, 1 H, *J* = 8.4 Hz, Ar**H**), 6.98-6.97 (d, 1 H, *J* = 4.0 Hz, Ar**H**), 6.86-6.84 (dd, 1 H, *J* = 1.6 Hz, *J* = 2.0 Hz, Ar**H**), 6.46 (s, 4 H, Ar**H**), 5.37-5.36 (d, 4 H, *J* = 2.8 Hz, ArC**H**$_2$-triazole), 5.22-5.21 (d, 4 H, *J* = 6.8 Hz, ArOC**H**$_2$-triazole), 4.22 (s, 2 H, ArC**H**$_2$N$_3$), 3.93-3.87 (m, 12 H, 6 ArOC**H**$_2$), 1.79-1.70 (m, 12 H, 6 ArOCH$_2$C**H**$_2$), 1.45-1.40 (m, 12 H, 6 ArOCH$_2$CH$_2$C**H**$_2$), 1.35-1.24 (m, 96 H, 48 C**H**$_2$), 0.89-0.86 (t, 18 H, *J* = 6.8 Hz, 6 C**H**$_3$).

IIEN^6/14: Yield: 655 mg, 92%, colourless solid. ^{1}H NMR (CDCl$_3$, 400 MHz): *δ* (ppm): 7.59-7.58 (d, 2 H, *J* = 4.4 Hz, triazole-**H**), 7.02-7.00 (d, 1 H, *J* = 8.4 Hz, Ar**H**), 6.98-6.97 (d, 1 H, *J* = 4.0 Hz, Ar**H**), 6.86-6.84 (dd, 1 H, *J* = 1.6 Hz, *J* = 2.0 Hz, Ar**H**), 6.46 (s, 4 H, Ar**H**), 5.37-5.36 (d, 4 H, *J* = 2.8 Hz, ArC**H**$_2$-triazole), 5.22-5.21 (d, 4 H, *J* = 6.8 Hz, ArOC**H**$_2$-triazole), 4.22 (s, 2 H, ArC**H**$_2$N$_3$), 3.93-3.87 (m, 12 H, 6 ArOC**H**$_2$), 1.79-1.70 (m, 12 H, 6 ArOCH$_2$C**H**$_2$), 1.45-1.40 (m, 12 H, 6 ArOCH$_2$CH$_2$C**H**$_2$), 1.35-1.24 (m, 120H, 60 C**H**$_2$), 0.89-0.86 (t, 18 H, *J* = 6.8 Hz, 6 C**H**$_3$).

2.7 Synthesis of 4,4'-dihydroxydiphenylmethane 9[S7]

Compound 4,4-dihydroxybenzophenone **8** (1 g, 4.67 mmol), LiAlH$_4$ and AlCl$_3$ were dissolved in dry THF (80 mL). The mixture was stirred 48 h at 65 °C. The solvent

was removed in *vacuo*. The residue was extracted with ethyl acetate (2 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether/ethyl acetate = 3 : 1). Yield: 635 mg, 68%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.04-7.02 (d, 4 H, J = 8.4 Hz, Ar**H**), 6.76-6.74 (d, 4 H, J = 8.4 Hz, Ar**H**), 4.59 (s, 2 H, ArO**H**), 3.84 (s, 2 H, ArC**H**$_2$Ar).

2.8 Synthesis of compound 10

Compound 4,4'-dihydroxydiphenylmethane **9** (400 mg, 2.0 mmol), propargyl bromide (708 mg, 6.0 mmol) and KOH (448 mg, 8.0 mmol) were dissolved in dry acetone (10 mL) under a nitrogen atmosphere. The mixture was refluxed over night. The solvent was removed in *vacuo*. The residue was extracted with ethyl acetate (2 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (petroleum ether/ethyl acetate = 10 : 1). Yield: 486 mg, 88%, light yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.13-7.10 (m, 4 H, Ar**H**), 6.92-6.89 (m, 4 H, Ar**H**), 4.68-4.66 (m, 4 H, ArOC**H**$_2$), 3.89-3.88 (d, 2 H, J = 3.2 Hz, ArC**H**$_2$Ar), 2.53-2.51 (m, 2 H, alkyne-**H**).

2.9 General procedure for the synthesis of IE^m/n and IIE^m/n

Compound **IEN^m/n** and **IIEN^m/n** (0.2 mmol), compound **10** (0.085 mmol) were dissolved in THF (8 mL), tert-butyl alcohol : H_2O = 1 : 1 (2 mL), $CuSO_4 \cdot 5H_2O$ (0.062 mmol) and sodium ascorbate (0.114 mmol) were added. The mixture was stirred over night at 45 °C. The solvent was removed in *vacuo*. The residue was extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4, then the solvent was removed in *vacuo*. The residue was purified by chromatography (CH_2Cl_2: ethyl acetate = 60 : 1).

IE^3/14: Yield: 131mg, 77%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.95 (s, 2 H, triazole-**H**), 7.64-7.62 (d, 4 H, J = 9.2 Hz, Ar**H**), 7.12-7.08 (t, 8 H, J = 8.8 Hz, Ar**H**), 6.95-6.93 (d, 4 H, J = 8.8 Hz, Ar**H**), 6.62 (s, 4 H, Ar**H**), 5.26 (s, 4 H, ArOC**H**$_2$-triazole), 5.00 (s, 4 H, ArOC**H**$_2$Ar), 3.99-3.94 (m, 12 H, 6 ArOC**H**$_2$), 3.88 (s, 2 H, ArC**H**$_2$Ar), 1.83-1.73 (m, 12 H, 6 ArOCH$_2$C**H**$_2$), 1.52-1.40 (m, 12 H, 6 ArOCH$_2$CH$_2$C**H**$_2$), 1.35-1.25 (m, 120 H, 60 C**H**$_2$), 0.89-0.86 (t, 18 H, J = 6.6 Hz, 6 C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 159.12(2C), 156.72(2C), 153.53(4C), 145.04(2C), 138.30(2C), 134.41(2C), 131.24(2C), 130.76(2C), 130.00(4C), 122.35(4C), 121.10(2C), 115.85(4C), 114.89(4C), 106.29(4C), 73.59(2C), 70.94(2C), 69.32(4C), 62.27(2C), 40.27(1C), 32.05, 30.47, 29.87, 29.83, 29.79, 29.78, 29.55, 29.50, 29.49, 26.26, 26.24, 22.81, 14.24(multi carbons in alkyl chain). Elemental Analysis calcd (%) for $C_{129}H_{206}N_6O_{10}$ (1999.58): C 77.43, H 10.38, N 4.20; found: C 77.92, H 10.44, N 4.22.

IIE^6/10: Yield: 194mg, 72%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.60-7.58 (d, 4 H, J = 6.8 Hz, triazole-**H**), 7.54 (s, 2H, triazole-**H**), 7.06-7.04 (d, 4 H, J = 8.8 Hz, Ar**H**), 7.00-6.98 (d, 4 H, J = 8.0 Hz, Ar**H**), 6.89-6.87 (d, 4 H, J = 8.8 Hz, Ar**H**), 6.84-6.82 (d, 2 H, J = 8.0 Hz, Ar**H**), 6.47 (s, 8 H, Ar**H**), 5.39 (s, 4 H, ArC**H**$_2$-triazole), 5.36-5.35 (d, 8 H, J = 2.8 Hz, 2 ArC**H**$_2$-triazole), 5.18-5.13 (t, 12 H, J = 8.4 Hz, ArOC**H**$_2$), 3.93-3.86 (m, 24 H, 12 ArOC**H**$_2$), 3.83 (s, 2 H, ArC**H**$_2$Ar), 1.77-1.70 (m, 24 H, 12 ArOCH$_2$C**H**$_2$), 1.45-1.41 (m, 24 H, 12 ArOCH$_2$CH$_2$C**H**$_2$), 1.29-1.23 (m, 144 H, 72 C**H**$_2$), 0.89-0.85 (t, 36 H, J = 6.8 Hz, 12 C**H**$_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.77(2C), 153.73(6C), 149.06(2C), 148.77(2C), 144.80(2C), 144.26(2C), 143.89(2C), 138.65(2C), 134.31(2C), 129.94(6C), 129.54(4C), 128.34(2C), 123.46(2C), 123.22(2C), 122.79(2C), 122.04(2C), 115.60(4C), 114.90(6C), 106.95(8C), 73.62(6C), 69.41(8C), 63.64(2C), 63.43(2C), 62.24(2C), 54,66(2C), 53.98(2C), 40.26(1C), 32.08, 32.06, 30.49, 29.89, 29.83, 29.79, 29.74, 29.58, 29.54, 29.50, 26.26, 22.83, 14.25(multi carbons in alkyl chain). Elemental Analysis calcd (%) for $C_{193}H_{306}N_{18}O_{18}$ (3164.36): C 73.20, H 9.74, N 7.96; found: C 73.65, H 9.80, N 8.01.

IIE^6/12: Yield: 247mg, 83%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.60-7.58 (d, 4 H, J = 6.0 Hz, triazole-**H**), 7.54 (s, 2 H, triazole-**H**), 7.06-7.04 (d, 4 H, J = 8.4 Hz, Ar**H**), 7.01-6.99 (d, 4 H, J = 8.8 Hz, Ar**H**), 6.89-6.87 (d, 4 H, J = 8.8 Hz, Ar**H**), 6.84-6.82 (d, 2 H, J = 8.4 Hz, Ar**H**), 6.47 (s, 8 H, Ar**H**), 5.40 (s, 4 H, ArC$\mathbf{H}_2$-triazole), 5.36-5.35 (d, 8 H, J = 2.4 Hz, ArC$\mathbf{H}_2$-triazole), 5.18-5.13 (t, 12 H, J = 8.6 Hz, ArOC$\mathbf{H}_2$), 3.92-3.86 (m, 24 H, 12 ArOC$\mathbf{H}_2$), 3.83 (s, 2 H, ArC$\mathbf{H}_2$Ar), 1.77-1.68 (m, 24 H, 12 ArOCH$_2$C$\mathbf{H}_2$), 1.45-1.41 (m, 24 H, 12 ArOCH$_2$CH$_2$C$\mathbf{H}_2$), 1.30-1.22 (m, 192 H, 96 C$\mathbf{H}_2$), 0.89-0.86 (t, 36 H, J = 6.8 Hz, 12 C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.76(2C), 153.72(6C), 149.03(2C), 148.75(2C), 144.79(2C), 144.23(2C), 143.88(2C), 138.63(2C), 134.30(2C), 129.93(6C), 129.50(4C), 128.32(2C), 123.45(2C), 123.21(2C), 122.78(2C), 122.03(2C), 115.58(4C), 114.89(6C), 106.92(8C), 73.61(4C), 69.39(8C), 63.63(2C), 63.41(2C), 62.23(3C), 54,64(3C), 53.97(2C), 40.26(1C), 32.07, 30.49, 29.89, 29.85, 29.80, 29.59, 29.53, 26.26, 22.83, 14.25(multi carbons in alkyl chain). Elemental Analysis calcd (%) for $C_{217}H_{354}N_{18}O_{18}$ (3500.73): C 74.40, H 10.19, N 7.20; found: C 74.87, H 10.25, N 7.24.

IIE^6/14: Yield: 238mg, 73%, white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm): 7.60-7.58 (d, 4 H, J = 6.0 Hz, triazole-**H**), 7.54 (s, 2 H, triazole-**H**), 7.06-7.04 (d, 4 H, J = 8.4 Hz, Ar**H**), 7.01-6.99 (d, 4 H, J = 8.8 Hz, Ar**H**), 6.89-6.87 (d, 4 H, J = 8.4 Hz, Ar**H**), 6.84-6.82 (d, 2 H, J = 8.4 Hz, Ar**H**), 6.47 (s, 8 H, Ar**H**), 5.40 (s, 4 H, ArC$\mathbf{H}_2$-triazole), 5.36 (s, 8 H, ArC$\mathbf{H}_2$-triazole), 5.18-5.13 (t, 12 H, J = 8.2 Hz, ArOC$\mathbf{H}_2$), 3.92-3.86 (m, 24 H, 12 ArOC$\mathbf{H}_2$), 3.83 (s, 2 H, ArC$\mathbf{H}_2$Ar), 1.75-1.69 (m, 24 H, 12 ArOCH$_2$C$\mathbf{H}_2$), 1.45-1.42 (m, 24 H, 12 ArOCH$_2$CH$_2$C$\mathbf{H}_2$), 1.25 (m, 240 H, 120 C$\mathbf{H}_2$), 0.89-0.86 (t, 36 H, J = 6.6 Hz, 12 C$\mathbf{H}_3$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 156.60(2C), 153.57(6C), 148.86(2C), 148.58(2C), 144.64(2C), 144.09(2C), 143.73(2C), 138.43(2C), 134.16(2C), 129.80(6C), 129.40(4C), 128.15(2C), 123.34(2C), 123.10(2C), 122.66(2C), 121.88(2C), 115.36(4C), 114.73(6C), 106.73(8C), 74.26(2C), 74.00(2C), 73.47(4C), 69.23(8C), 63.44(2C), 63.23(2C),

62.07(2C), 54,52(2C), 53.84(2C), 40.12(1C), 31.94, 30.35, 30.24, 29.77, 29.74, 29.39, 29.25, 26.13, 26.01, 22.71, 14.13(multi carbons in alkyl chain). Elemental Analysis calcd (%) for $C_{241}H_{402}N_{18}O_{18}$ (3837.11): C 75.38, H 10.55, N 6.57; found: C 75.82, H 10.61, N 6.61.

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