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Supplementary Information

For

The synthesis of conjugated microporous polymers via nucleophilic substitution of hydroquinone with cyanuric chloride and hexachlorocyclotriphosphazene for sensing to 2,4-dinitrophenol and 2,4,6-trinitrophenol

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S1. Experimental Section

S1-1. Materials

Hydroquinone, cyanuric chloride (CC), and trienthylamine (TEA) were purchased from Aladdin. Hexachlorocyclotriphosphazene (phosphonitrilic chloride trimer, HCCP) was obtained from Shanghai Shaoyuan reagent Co., Ltd. All chemicals were used without any purification. All of the chemicals were purchased from commercial suppliers and used without further purification as commercially available unless otherwise noted. Solvents were dried and distilled following a standard procedure.

S 1-2. Synthesis of the CMPs

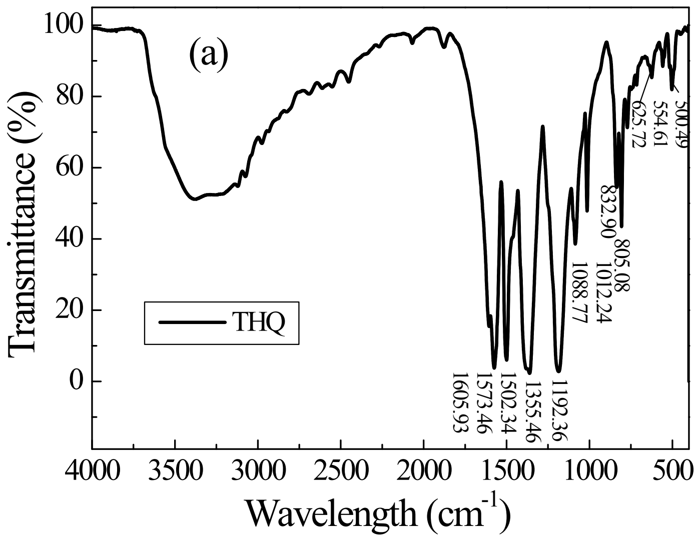
S 1-2-1. Synthesis of THQ

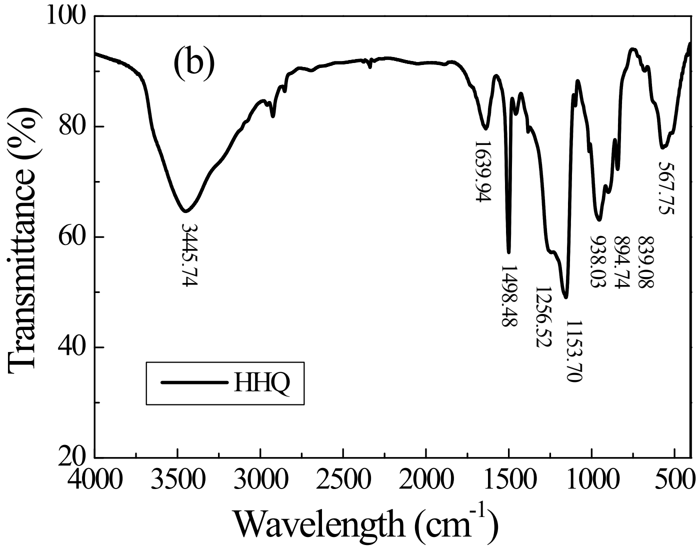
Cyanuric chloride (8.0 mmol, 1.4753 g) was dissolved in 50 mL of dioxane in a 250 mL three-neck flasks. Then hydroquinone (12.0 mmol, 1.3213 g), triethylamine (TEA) (30 mmol, 4.16 mL), and dioxane (100 mL) were added to the flasks. The reaction was carried at room temperature for two hours, then refluxing at 120 ^{o}C for 5d under nitrogen protection. The reaction mixture was cooled and the solid was removed by filtration and washed with 10% Na_2CO_3, distilled water, ethanol, and acetic ether three times for each. The powder was then Solxet extracted with THF and ethanol for 24 hours for each. The brown powder was dried at 50 °C under vacuum for 24 h to give the product. Yield: 53.75 %. Elemental analysis for $C_{25}H_{18}N_6O_6$

calculated (%): C, 60.24; H, 3.64; N, 16.85 and found (%): C, 58.00; H, 3.408; N, 17.96.

S 1-2-2. Synthesis of HHQ

HHQ was obtained as light brown colored powder using the same procedures. HCCP (4.0 mmol, 1.3906 g), hydroquinone (12 mmol, 1.3213 g), TEA (30 mmol, 4.16 mL), and dioxane (100 mL) (yield: 71.98 %). Elemental analysis for $C_{21}H_{24}N_3O_3P_3$ calculated (%): C, 54.91; H, 5.27; N, 9.15 and found (%): C, 50.73; H, 4.459; N, 10.20.





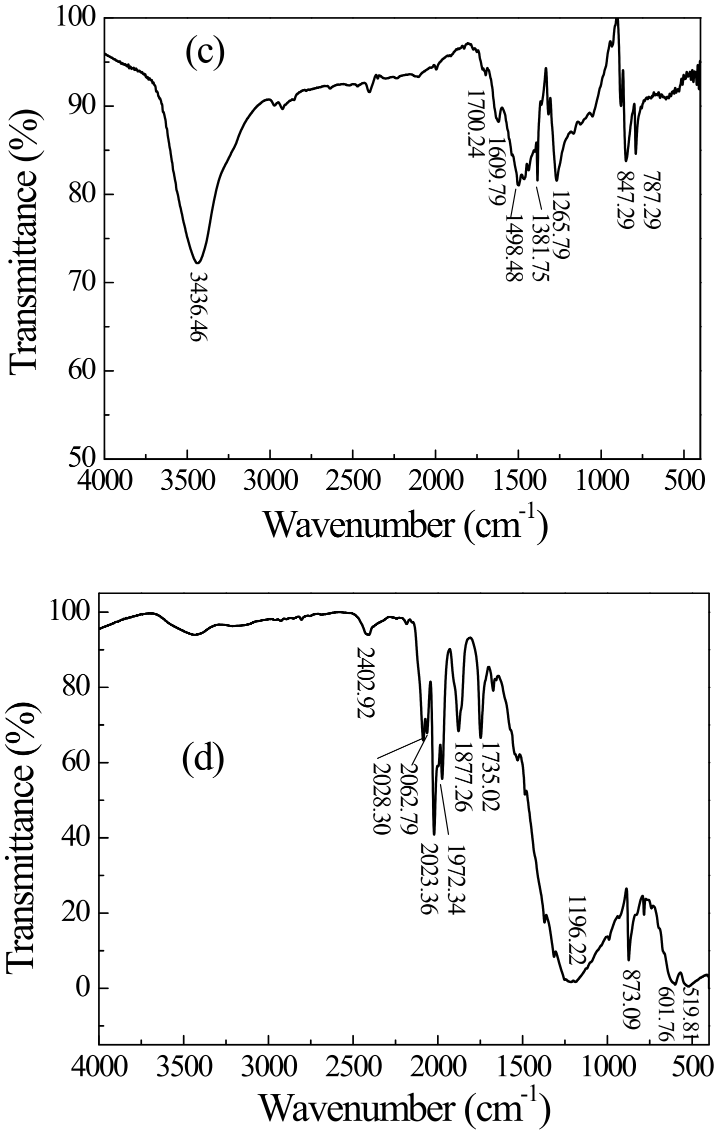


Fig. S1. FT-IR spectra of CMPs and monomers. (a) THQ, (b) HHQ, (c) CC, and (d) HCCP.

S1. 3. Methods

Infrared spectra were recorded on an iS50 FT-IR spectrometer (400 to 4000 cm^{-1}) by using KBr pellets. Solid-state ^{13}C CP/MAS NMR measurements were recorded on a Bruker AVANCE III 400 WB spectrometer at a MAS rate of 5 kHz and a CPcontact time of 2 ms. UV−Vis spectra were recorded on an UV-2501PC spectrometer. Elemental analyses were carried out on a VARIO ELIII cube analyzer. Scanning electron microscopy was performed on a S-3400N microscope. Thermogravimetri analysis (TGA) measurements were performed on a CDR-4P TGA under N_2, by heating to 800 °C at a rate of 10 °C min^{-1}. X-ray diffraction (XRD) data were recorded on a XRD 600 diffractometer by depositing powder on glass substrate, from 2θ =5° to 90° with 0.02° increment. The Brunauer-Emmett-Teller (BET) method was utilized to calculate specific surface area and pore volume, the Saito-Foley (SF) method was applied for estimation of pore size distribution. Fluorescence spectra were recorded at room temperature using a Hitachi F-4500 spectrophotometer. Samples were prepared as follows: dried CMPs powder (10 mg) ground with an agate mortar was added to 10 mL of organic solvents. After the resulting mixture was well dispersed with ultrasound, the dispersion colloid was obtained.

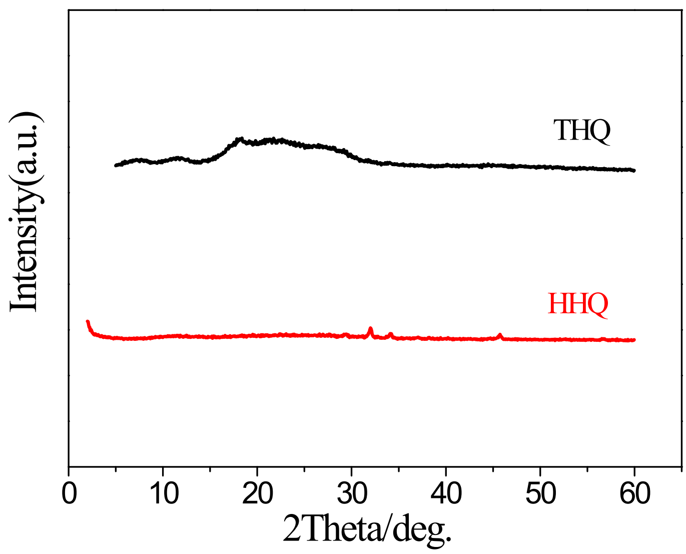


Fig. S2. XRD patterns of THQ (black) and HHQ (red).

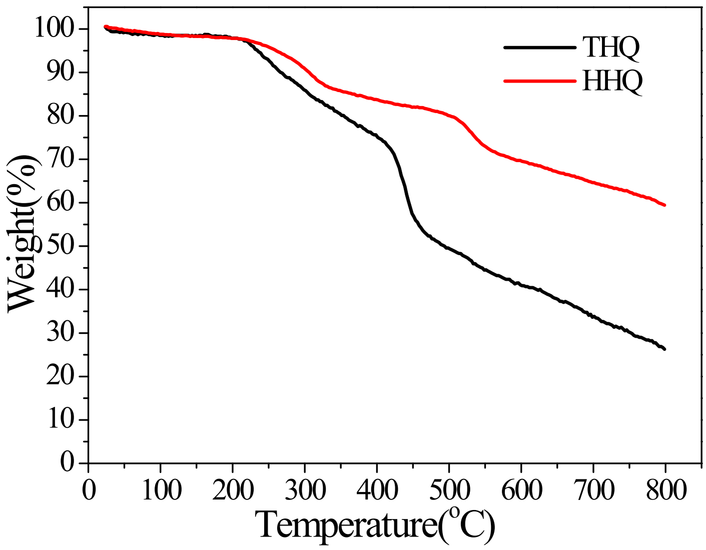


Fig. S3. TGA analysis data of THQ and HHQ. Data collected by heating at 10 ^oC min^{-1} under a nitrogen atmosphere.

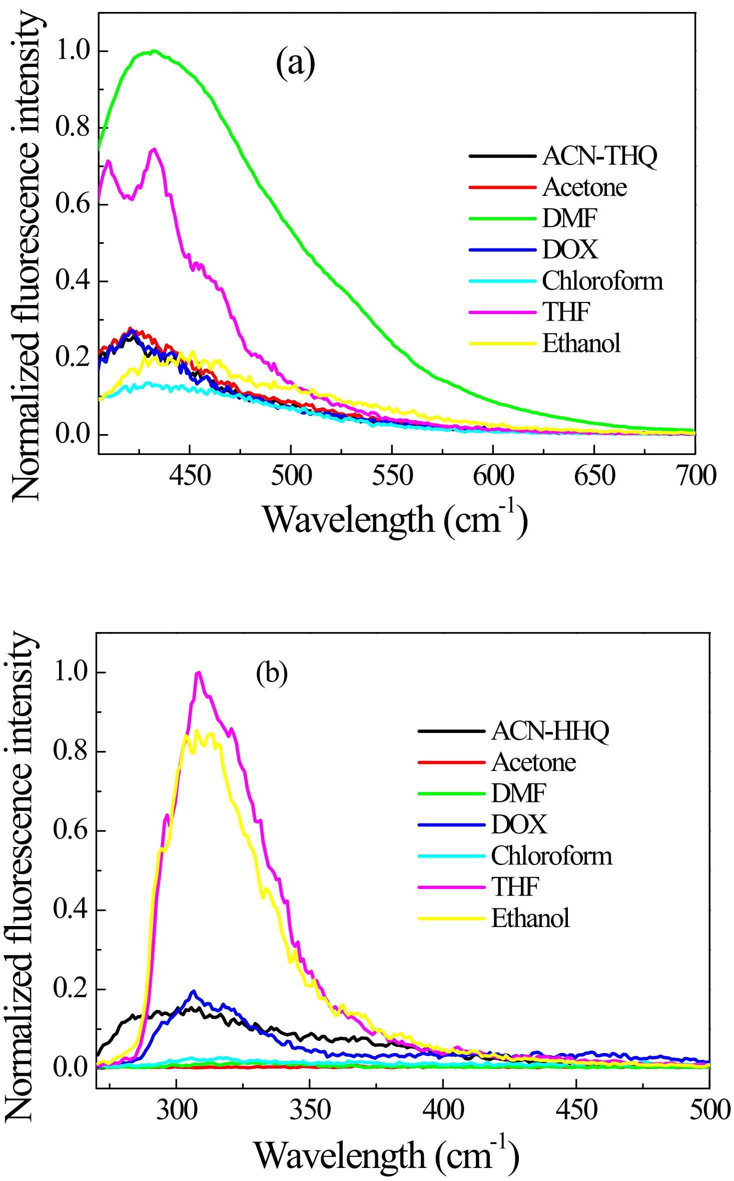
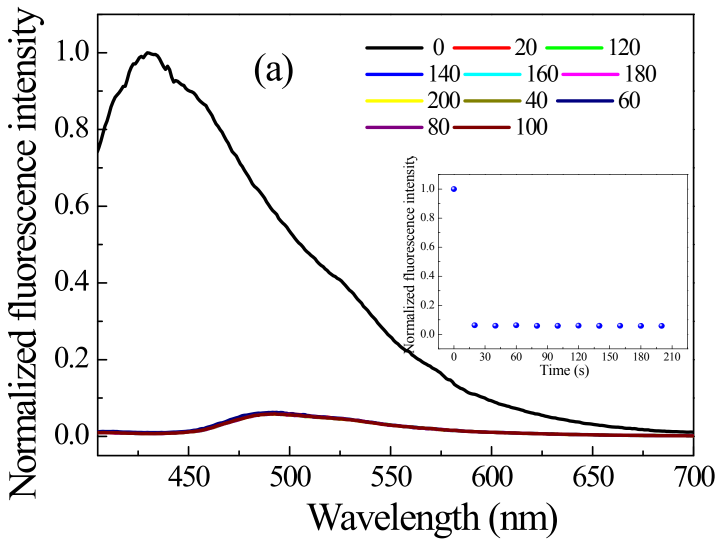


Fig. S4. Fluorescence spectra of (a) THQ and (b) HHQ in various solvents (1.0 mg mL^{-1}, λex=375 and 260 nm).



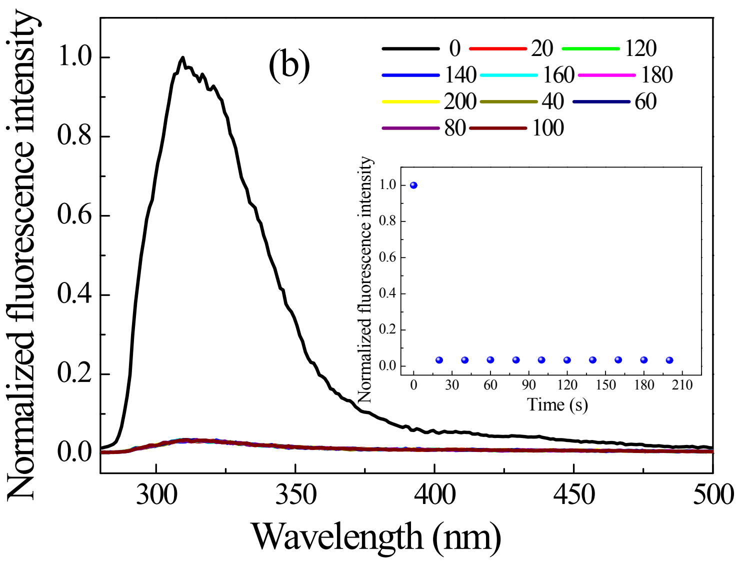


Fig. S5. Fluorescence spectral changes of (a) THQ dispersed in DMF (1.0 mg mL^{-1}, $\lambda ex=375$) and (b) HHQ dispersed in THF (1.0 mg mL^{-1}, $\lambda ex= 260$ nm) upon addition of DNP and TNP. Inserts: the evolution of maximum fluorescence intensity as a function of time.

S2. The detail experiment and calculation processes for limit of detections (LODs).

S2-1. The experiments of LODs for DNP and TNP.

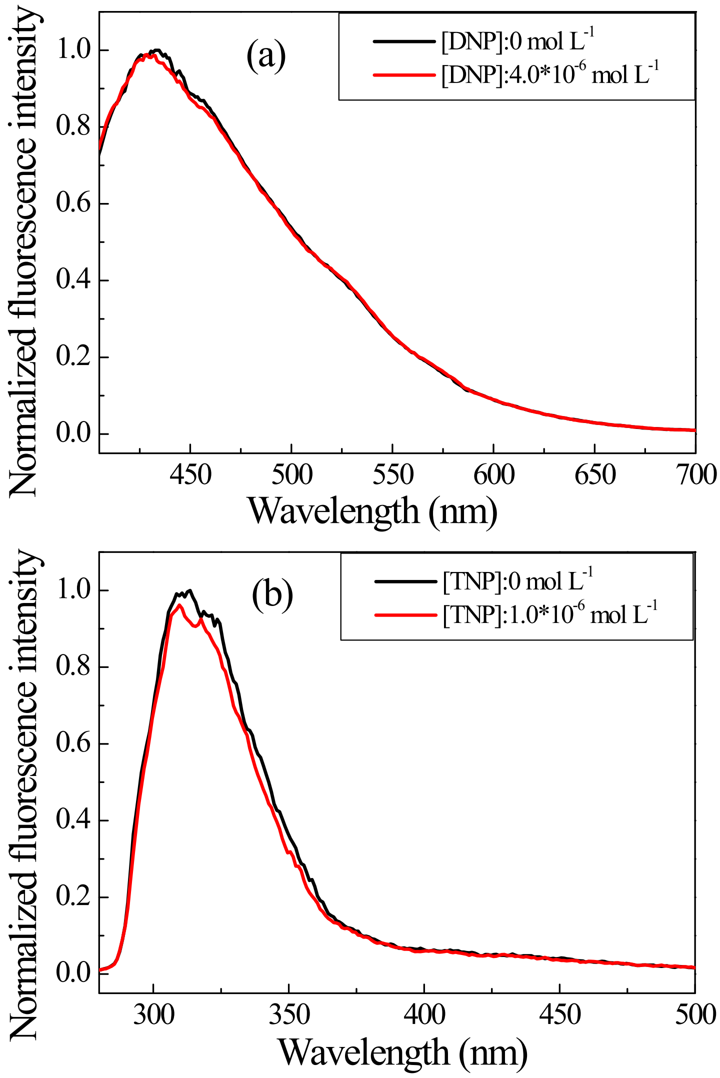


Fig. S6. The experiments for LODs of DNP and TNP.

S2-2. The detail calculation processes of LODs.

S2-2-1.The calculation for LOD of DNP.

The LOD of DNP: 0.1 mol L^{-1}, 0.08μL

$I_0/I=6.4969\times10^4[DNP]+1.1002$, R=0.9991, 0-$1\times10^{-4}$ mol L^{-1}

$S=0.08\mu L\times10^{-6}\times0.1/2.0\times10^{-3}=4.0\times10^{-6}$ mol L^{-1}

$LOD = 3S/\rho = 3\times4.0\times10^{-6}/6.4964\times10^{4} = 1.85\times10^{-10}$ mol L^{-1}

S2-2-2.The calculation for LOD of TNP.

The LOD of TNP: 0.1 mol L^{-1}, 0.02μL

$I_0/I = 23.037\times10^{4}[TNP] - 0.1985$, $R=0.9940$, $0\text{-}5\times10^{-5}$ mol L^{-1}

$S = 0.02\mu L\times10^{-6}\times0.1/2.0\times10^{-3} = 1.0\times10^{-6}$ mol L^{-1}

$LOD = 3S/\rho = 3\times1.0\times10^{-6}/23.037\times10^{4} = 1.30\times10^{-11}$ mol L^{-1}

Table S1. Summary of K_{sv} and LODs of other materials for the determination of

DNP.

materials	BET ($m^2\ g^{-1}$)	Methods or K_{sv} ($L\ mol^{-1}$)	LODs ($mol\ L^{-1}$)	Refs
-	-	SPE and UHPLC –QTR AP® MS	1.85×10^{-10} (34 ng/l)	*Anal. Bioanal. Chem., 2013, 405, 5875–5885.*
SBA-15 CMK-3	660 1400	CMK-3-GC –MS method	1.09×10^{-8} (0.002 μg mL^{-1})	*Anal. Chim. Acta, 2011, 695, 58–62.*
GO-MIP/GCE composites	-	electrochemical sensor	4×10^{-7} (0.4 μM)	*Sensor. Actuat. B-Chem., 2012, 171–172, 1151–1158.*
SPE-MIPs	-	fluorescence detection	1×10^{-9} (1 nmol L^{-1})	*Chinese Chem. Lett., 2014, 25, 1492–149.*
Dialysed caramel	-	fluorescence detection	1.4×10^{-7} (0.14μM)	*Talanta, 2019, 197, 159–167.*
MOFs	-	-	-	*J. Mater. Chem. A 2015, 3, 22369–22376.*
proximate pyrene units	-	fluorescence detection 1×10^{4}	-	*Tetrahedron Lett., 2015,56, 2311–2314.*
TTPTh	564.97	1.10×10^{4}	5.47×10^{-10}	*New J. Chem., 2020, 44, 19663-19671.*
DBTh	416.99	5.76×10^{4}	1.56×10^{-10}	
TBTh	521.30	9.59×10^{3}	9.38×10^{-9}	
COF-BABD-DB	568.6	9.59×10^{3}	-	*Chem. Commun., 2018, 54, 2308-2311.*
COF-BABD-BZ	750.5	1.50×10^{4}	-	

THQ	71.55	3.20×10^{4}	1.85×10^{-10}	*This work.*

Table S2. Summary of K_{sv} and LODs of other CMPs for the determination of TNP.

materials	BET ($m^2\ g^{-1}$)	Methods or K_{sv} ($L\ mol^{-1}$)	LODs ($mol\ L^{-1}$)	Refs
TDPDB	592.18	1.55×10^{4}	1.93×10^{-11}	*Polym. Adv. Technol. 2020, 31(6), 1388–1394.*
CK-CMP	-	9.9×10^{4}	-	*Inorg. Chem. Comm., 2019, 107, 107453*
^{i}PrTAPB -Azo-COP	395	1.1×10^{4}	-	*J. Chem. Sci., 2018. 130(1), 1-14.*
HPP-2	747	2.41×10^{4}	17.67 ppb	*Sensor. Actuat. B-Chem., 2018, 265, 476–487.*
CMP-LS1	493	5.05×10^{4}	-	*New J. Chem., 2018, 42, 9482–9487.*
CMP-LS2	1576	3.70×10^{4}	-	
PNT-4	1311.54	6.22×10^{5}	2.36×10^{-9}	*Sensor. Actuat. B-Chem., 2018, 274, 102–109.*
PNT-5	817.32	5.08×10^{5}	3.12×10^{-9}	
PNT-6	433.24	2.38×10^{5}	5.52×10^{-9}	
COP-612	48.80	2.51×10^{5}	-	*Sensor. Actuat. B-Chem., 2017, 243, 753–760.*
DTF	705.27	2.08×10^{3}	7.22×10^{-7}	*Talanta, 2017, 165, 282–288.*
PTPATTh	594	5.00×10^{3}	3.01×10^{-9}	
PTPATCz	894	4.28×10^{3}	7.01×10^{-9}	*Sensor. Actuat. B-Chem.,*

TTPB	222.25	1.29×10^{3}	8.14×10^{-9}	*2017,244, 334–343*
				J. Mater. Chem. A., 2017, 5,
DCZP	688	3.94×10^{3}	-	*7612–7617.*
DCZN	97	6.63×10^{3}	-	*J Mater Sci.,*
DBQP	355.76	9.02×10^{4}	3.33×10^{-13}	*2016, 51, 4104–4114.*
DBQN	25.48	1.79×10^{4}	2.48×10^{-13}	*Micropor.Mesopor. Mater.,*
COP-401	-	8.3×10^{4}	-	*2016, 231, 92–99.*
COP-301	-	2.6×10^{5}	-	*J. Mater. Chem. A, 2015, 3,*
FL-SNWDPP	750	5.3×10^{4}	-	*92–96*
-0.11				*J. Mater. Chem. C, 2015, 3,*
polyTPECz film	1020	6.4×10^{4}		*6876–6881*
				Angew. Chem. Int. Ed. 2015,
COP-61	1302	2.40×10^{5}	1 ppm	*54, 11540–11544*
COP-62	1208	1.82×10^{5}	1 ppm	*J. Mater. Chem. C, 2015, 3,*
COP-63	931	8.04×10^{4}	1 ppm	*8490–8494*
COP-64	716	9.79×10^{4}	1 ppm	
COP-65	869	6.80×10^{4}	1 ppm	
P2	39	2.1×10^{3}	-	
P3	143	7.6×10^{4}	-	*Polym. Chem., 2015, 6,*
COP-3	1869	1.45×10^{4}	-	*3775–3780.*
COP-4	2015	3.93×10^{3}	-	*Macromol. Rapid Commun.*
HHQ	24.16	2.30×10^{5}	1.30×10^{-11}	*2012, 33, 1184−1190.*

	This work.