Electronic Supplementary Information

Gallic ester-based phase-selective gelators

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Experimental Section

Materials and Instruments

Gallic acid was purchased from Alfa Aesar. All the other solvents and chemicals used were produced by Tianjin Bodi Chemical Holding Co. Ltd, China (reagent grade) and used as received. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker AM-500 spectrometer. The IR spectra were conducted on a Shimadzu FTIR-8900 spectrometer. The elemental analysis was performed on a Elementar Vario EL III elemental analyzer. The DSC spectra were conducted on NETZSCH DSC 200 F3. The SEM spectra were obtained with a SHITACHI S-4800. The TEM spectra were obtained with a HITACHI H-765 transmission electron microscope. The XRPD spectra were obtained with a Bruker D8 ADVANCE. Analysis of aniline in water was performed by high performance liquid chromatography on Waters 600E-2998.

All compounds were synthesized according to the literature procedure.[1]

Characterizations of new compounds

Butyl 3,4,5-tris(hexadecyloxy)benzoate (**1c**): m.p.: 45-46 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 2H), 4.29 (t, J = 7.0 Hz, 2H), 4.00 (t, J = 6.5 Hz, 6H), 1.71-1.78 (m, 8H), 1.44-1.48 (m, 8H), 1.21-1.28 (m, 72H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6, 152.7, 142.4, 125.1, 108.1, 73.5, 69.4, 65.4, 64.8, 33.7, 33.0, 32.1, 30.7, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 22.8, 21.2, 14.3. IR (cm^{-1}, KBr): 2916, 2849, 1709, 1589, 1504, 1466, 1225, 1125, 721.

Pentyl 3,4,5-tris(hexadecyloxy)benzoate (**1d**): m.p.: 44-46 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 2H), 4.29 (t, *J* = 7.0 Hz, 2H), 4.01 (t, *J* = 6.5 Hz, 6H), 1.70-1.77 (m, 8H), 1.44-1.48 (m, 8H), 1.21-1.28 (m, 74H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.6, 152.7, 142.4, 125.1, 108.1, 73.5, 69.4, 65.4, 64.8, 33.7, 33.0, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 28.7, 28.3, 26.2, 22.8, 21.2, 14.3. IR (cm^{-1}, KBr): 2916, 2848, 1710, 1586, 1503, 1430, 1225, 1124, 722.

Dodecyl 3,4,5-tris(hexadecyloxy)benzoate (**1e**): m.p.:49-50 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.24 (s, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.71-1.78 (m, 8H), 1.44-1.48 (m, 8H), 1.21-1.28 (m, 88H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.8, 153.1, 142.4, 125.4, 108.1, 73.8, 73.5, 71.3, 69.1, 65.2, 64.8, 33.6, 33.1, 32.1, 30.7, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.9, 28.8, 28.7, 26.4, 26.2, 26.1, 25.5, 22.8, 21.3, 14.2. IR (cm^{-1}, KBr): 2918, 2849, 1716, 1587, 1500, 1466, 1220, 1121, 722.

Tetradecyl 3,4,5-tris(hexadecyloxy)benzoate (**1f**) : m.p.:54-56 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.24 (s, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.71-1.78 (m, 8H), 1.44-1.48 (m, 8H), 1.21-1.28 (m, 92H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.5, 152.9, 142.5, 125.3, 108.4, 73.5, 73.4, 71.3, 69.3, 65.5, 64.8, 33.7, 33.0, 32.2, 30.7, 30.4, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 28.8, 28.7, 26.4, 26.2, 26.1, 25.5, 22.8, 21.3, 14.2. IR (cm^{-1}, KBr): 2917,

2850, 1714, 1587, 1500, 1466, 1217, 1122, 724.

Hexadecyl 3,4,5-tris(hexadecyloxy)benzoate (**1g**) : m.p.:53-56 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 2H), 4.28 (t, *J* = 7.0 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.71-1.78 (m, 8H), 1.44-1.48 (m, 8H), 1.21-1.28 (m, 96H), 0.88 (t, *J* = 7.0 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.7, 152.9, 142.5, 125.2, 108.2, 73.6, 73.4, 71.1, 69.3, 65.3, 64.8, 33.7, 33.0, 32.1, 30.7, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 28.9, 28.8, 28.7, 26.4, 26.2, 26.1, 25.5, 22.8, 21.2, 14.3. IR (cm^{-1}, KBr): 2917, 2849, 1712, 1586, 1500, 1465, 1220, 1122, 722

Isopropyl 3,4,5-tris(hexadecyloxy)benzoate (**1h**) : m.p.:49-50 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.24 (s, 2H), 4.28 (s, 1H), 4.00 (t, *J* = 6.5 Hz, 6H), 1.71-1.78 (m, 6H), 1.44-1.48 (m, 6H), 1.37 (s, 6H), 1.21-1.28 (m, 72H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.7, 152.7, 142.6, 125.1, 108.1, 73.5, 69.2, 68.9, 66.6, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 23.7, 22.8, 14.3. IR (cm^{-1}, KBr): 2919, 2850, 1703, 1591, 1503, 1465, 1220, 1116, 723.

Phenyl 3,4,5-tris(hexadecyloxy)benzoate (**1i**) : m.p.:40-42 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.44 (d, *J* = 7.0 Hz, 2H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.28-7.29 (m, 3H), 5.35 (s, 2H), 3.98-4.02 (m, 6H), 1.70-1.83 (m, 6H), 1.43-1.49 (m, 6H), 1.24-1.28 (m, 72H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.7, 152.9, 142.5, 125.2, 108.2, 73.5, 69.2, 68.9, 66.5, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 23.7, 22.8, 14.3. IR (cm^{-1}, KBr): 2917, 2850, 1715, 1589, 1500, 1466, 1218, 1121, 721.

Cyclohexyl 3,4,5-tris(hexadecyloxy)benzoate (**1j**) : m.p.:48-49 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 2H), 4.96-5.01 (m, 1H), 3.99-4.03 (m, 6H), 1.93-1.96 (m, 2H), 1.71-1.85 (m, 10H), 1.43-1.48 (m, 10H), 1.21-1.28 (m, 72H), 0.88 (t, *J* = 7.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.0, 152.9, 142.4, 125.7, 108.2, 73.6, 73.2, 69.4, 33.7, 32.1, 31.8, 30.7, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 28.7, 26.3, 25.6, 23.9, 22.8, 14.3. IR (cm^{-1}, KBr): 2917, 2848, 1708, 1593, 1500, 1463, 1213, 1122, 729.

Hexadecyl 3,4,5-triethoxybenzoate (2b) : m.p.:65-67 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.25 (s, 2H), 4.27-4.29 (m, 2H), 3.99-4.02 (m, 6H), 1.35 (t, *J* = 7.0 Hz, 9H), 1.27 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.1, 152.3, 141.9, 124.7, 108.3, 71.8, 69.4, 63.2, 22.8, 17.8. IR (cm^{-1}, KBr): 2919, 2851, 1714, 1588, 1507, 1472, 1224, 1131, 717.

Ethyl 3,5-bis(hexadecyloxy)benzoate (**3a**) : m.p.:58-59 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.15 (d, *J* = 2.0 Hz, 2H), 6.65 (t, *J* = 2.0 Hz, 1H), 4.29-4.33 (m, 2H), 3.98 (t, *J* = 7.0 Hz, 4H), 1.74-1.81 (m, 4H), 1.41-1.44 (m, 4H), 1.30 (t, *J* = 7.0 Hz, 3H), 1.21-1.26 (m, 48H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 166.8, 152.6, 142.8, 124.0, 106.7, 73.5, 69.2, 62.3, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 23.7, 22.3, 14.3. IR (cm^{-1}, KBr): 2919, 2848, 1721, 1604, 1469, 1232, 1168, 718. Hexadecyl 4-(hexadecyloxy)benzoate (**4b**) : m.p.: 78-79 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ ppm 7.92 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 4.29 (t, *J* = 7.0 Hz, 2H), 3.99 (t, *J* = 7.0 Hz, 2H), 1.72-1.76 (m, 4H), 1.41-1.45 (m, 4H), 1.23-1.27 (m, 48H), 0.88 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm 165.4, 155.6, 143.7, 125.5, 107.3, 73.5, 69.2, 32.1, 30.5, 29.9, 29.8, 29.7, 29.6, 29.5, 26.2, 23.7, 22.3, 14.3. IR (cm^{-1}, KBr): 2917, 2846, 1723, 1608, 1463, 1228, 1165, 723.

Gelation and Gel Characterization:

Gelation method. Typically, gelator (10 mg) in required solvent (1mL) was heated until the solid was completely dissolved. The resulting solution was slowly allowed to cool to room temperature, and gelation was visually observed. A gel sample was obtained that exhibited no gravitational flow in inverted tube. All gels obtained are thermally reversible. Above their gelation temperature, the gels dissolved in the solvent, but could be returned to their original gel state upon cooling.

Gel-sol phase transition temperature (T_g). T_{gel} was determined by using a conventional "falling ball" method.[2] A small glass ball (weighing 0.10 g) was carefully placed on the top of the gel to be tested, which was produced in a test tube. The tube was slowly heated (0.5 °C min^{-1}) in a thermostated water bath. The temperature (T_{gel}) was noted when the ball fell to the bottom of the test tube.

Differential scanning calorimetry (DSC): Differential scanning calorimetry was carried out by using a NETZSCH 200 F3 DSC. A volume of 40 μL of gelator **1b** in hot aniline was placed into a large volume capsule (LVC) that was then sealed. The sample LVC pan was placed into the DSC apparatus together with an empty LVC pan as reference. The pans were cooled to -10 °C, and aged for 30 min at this temperature. Heating and cooling scans were then recorded from -10 – 70 °C at a scan rate of 1°C min^{-1}.

FTIR Measurement. The gel sample were measured on a Shimadzu FTIR-8900 spectrometer in an attenuated total reflection (ATR) way with ZnSe as sample slot. The samples were placed on a glass or a mica slice as a gel film, frozen in liquid nitrogen, and finally dried in vacuum conditions for 12-24 h.

Microscopy studies: Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) measurements were performed using a SHITACHI S-4800 and a HITACHI H-765 microscopes, respectively. A piece of gel was mounted on a glass slide or 300-mesh carbon-coated copper grid for SEM and TEM sampling, respectively, and dried for a few hours under vacuum before imaging.

Powder X-ray Diffraction. Powder diffraction patterns of neat gelator and xerogel (aniline, frozen in liquid nitrogen, and finally dried in vacuum conditions) of **1b** were recorded on Bruker D8 ADVANCE (Cu Kα radiation).

Analysis of aniline in water. Analysis of aniline in water was performed by high performance liquid chromatography (Waters 600E-2998) with Eclipse XDB-C8 (150 mm × 4. 6 mm, 5 μm).[3] The optimum condition was as follows: injection volume was 5 μL, flow rate was 1 mL /min, mobile phase was V(acetonitrile):V(water) = 40:60. The equation of linear regression of this method is $y=2.4985*10^{-7}x+0.01873$.

Table S1 Gelation properties of the gelators in the solvents[a]

	1a	1b	1c	1d	1h	1i	1j	2a	2b	3a	3b	4a	4b
n-Hexane	P	P	P	P	P	P	P	P	P	P	P	P	P

n-Heptane	P	P	P	P	P	P	P	P	P	P	P	P	P
Dichloro-methene	S	S	S	S	S	S	S	S	S	S	S	S	S
Chloroform	S	S	S	S	S	S	S	S	S	S	S	S	S
n-Heptane	P	P	P	P	P	P	P	P	P	P	P	P	P
Ethyl acetate	S	S	S	S	S	S	S	S	S	S	S	S	S
Ethyl acetoacetate	S	S	S	S	S	S	S	S	S	S	S	S	S
Methanol	P	P	P	P	P	P	P	P	P	P	P	P	P
Ethanol	P	P	P	P	P	P	P	P	P	P	P	P	P
Propanol	P	P	P	P	P	P	P	P	P	P	P	P	P
Isopropanol	P	P	P	P	P	P	P	P	P	P	P	P	P
n-Butanol	P	P	P	P	P	P	P	P	P	P	P	P	P
Pentanol	P	P	P	P	P	P	P	P	P	P	P	P	P
Aacetone	P	P	P	P	P	P	P	P	P	P	P	P	P
Butanone	P	P	P	P	P	P	P	P	P	P	P	P	P
3-Methyl-2-butanone	P	P	P	P	P	P	P	P	P	P	P	P	P
Diethyl ether	S	S	S	S	S	S	S	S	S	S	S	S	S
THF	S	S	S	S	S	S	S	S	S	S	S	S	S
DMF	P	P	P	P	P	P	P	S	S	S	S	S	S
Toluene	S	S	S	S	S	S	S	S	S	S	S	S	S
Ethylbenzene	S	S	S	S	S	S	S	S	S	S	S	S	S
Aniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
***o*-Toluidine**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
***m*-Toluidine**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
4-(tert-Butyl)aniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
2-Methoxyaniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
2-Ethoxyaniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
4-Ethoxyaniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
***m*-Chloroaniline**	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
2,3-Dimethylaniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S

2,4-Dimethylaniline	**G**	**G**	**G**	**G**	**G**	**G**	**G**	S	S	P	P	S	S
Pyridine	S	S	S	S	S	S	S	S	S	S	S	S	S
Morpholine	P	P	P	P	P	P	P	S	S	S	S	S	S
Quinoline	P	P	P	P	P	P	P	S	S	S	S	S	S
1,2-Diaminoethane	P	P	P	P	P	P	P	P	P	P	P	P	P
Triethylamine	P	P	P	P	P	P	P	P	P	P	P	S	S
DMSO	I	I	I	I	I	I	I	I	I	I	I	I	I
H_2O	I	I	I	I	I	I	I	I	I	I	I	I	I

[a] G: gelation, P: precipitation, I: insoluble, S: soluble. The gelation concentrations are 4 mg/ml.

	Blank	After gelation						
pH	7	1	3	5	7	9	11	13

Compounds	**1a**	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**
T_{gel}(º C)	41	43	27	30	--	--	--	28	26	34

Table S2 The T_{gel} of aniline gel **(**2 mg mL^{-1}**)**

Table S3 The T_{gel} against gelator **1b** concentration in aniline

mg mL^{-1}	**2**	**4**	**6**	**8**	**10**	**12**	**14**
T_{gel} (ºC)	43	47	50	52	52	52	52

Table S4 The residue aniline in water dependence on pH values

C (mg mL^{-1})	36.17	21.38	21.33	7.38	6.87	24.83	26.39	24.81

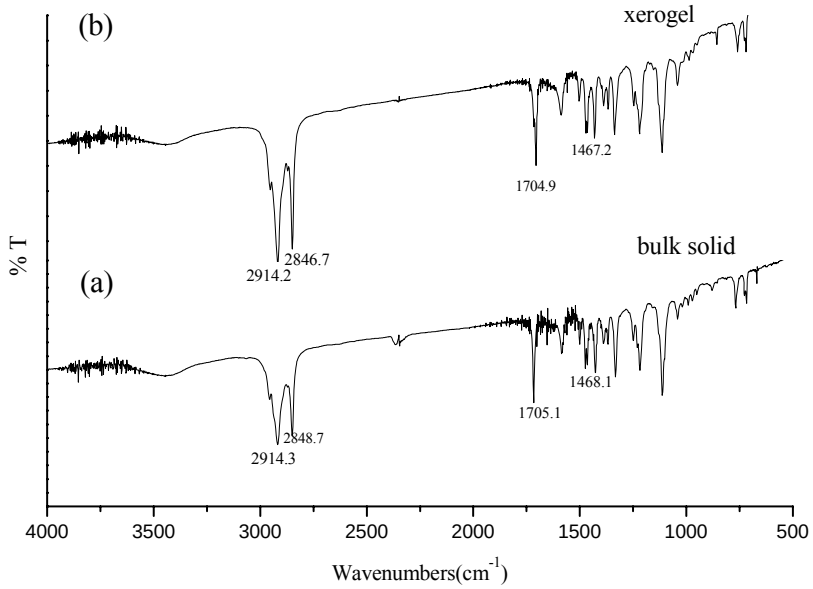

Fig. S1 FT-IR spectra of the xerogel of **1b** in aniline (a) and neat **1b** solid (b).

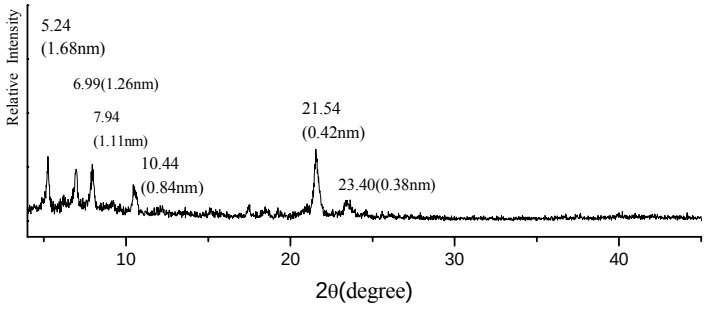

Fig. S2 XRD analysis of the xerogel of **1b** in aniline

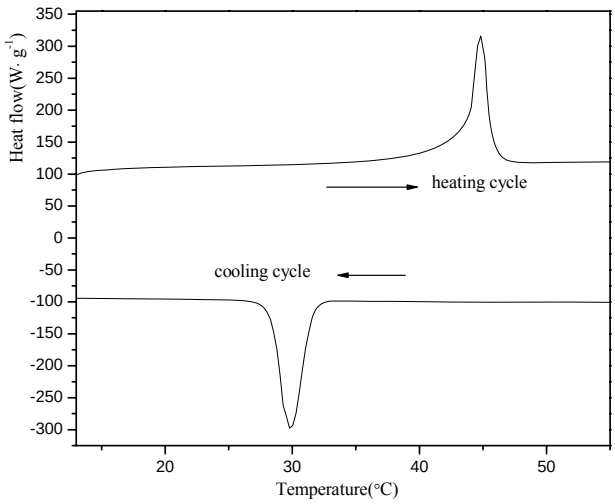

Fig. S3 Differential scanning calorimetry (DSC) heating (upper trace) and cooling (lower trace) scan of a gel of **1b** in aniline. (4 mg/mL, heating and cooling rate was 1 °C/ min).

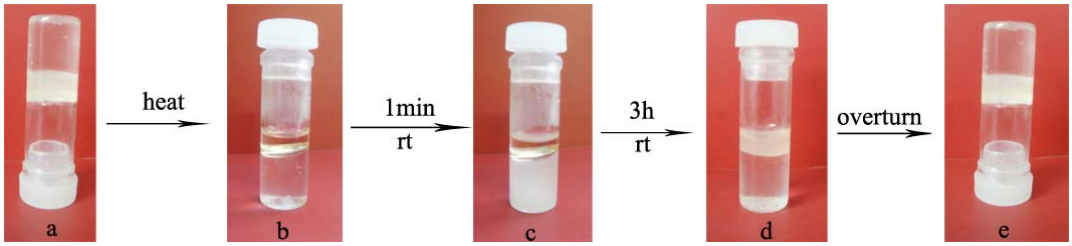

Fig. S4 The gelator **1b** exhibits phase-selective gelation of aniline liquid in the presence of water at rt.

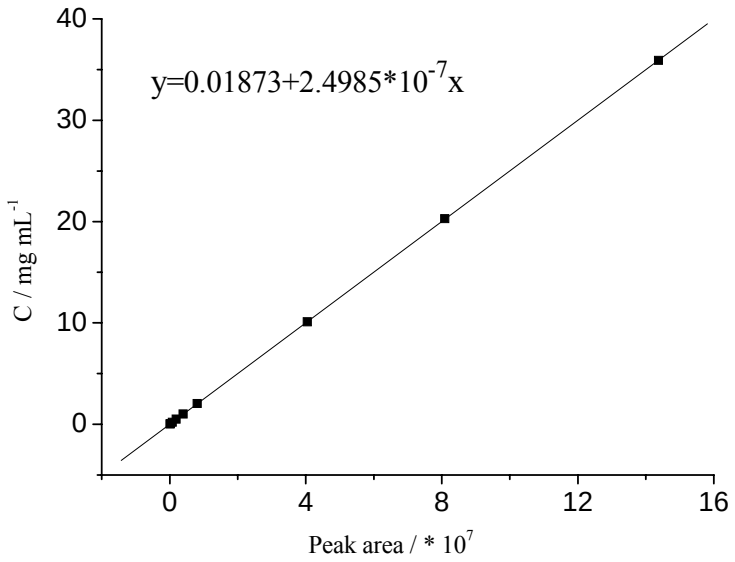

Fig. S5 Standard curve of concentration of **1b** (*y*-axis) vs peak area (*x*-axis).

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3 Environmental Protection Bureau of China. *Standard Methods for Examination of Water and Wastewater*, China Environmental Science Press, Beijing, 4th edn., 2002, pp. 548- 555