

*Supporting Information*

*for*

**Selective Cu(II) Sensing by a Versatile AIE Cyanostilbene-based Gels System**

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	<b><i>Contents</i></b>	<b><i>Page</i></b>
<b>1</b>	Materials and Methods	<b>S3</b>
<b>2</b>	Gelation test	<b>S3</b>
<b>3</b>	Rheology measurement	<b>S4</b>
<b>4</b>	Synthesis of <b>1-3</b>	<b>S5–S8</b>
<b>5</b>	<sup>1</sup> H and <sup>13</sup> C-NMR spectra of <b>1-4</b>	<b>S9-S12</b>
<b>6</b>	AIE properties of <b>1-3</b>	<b>S13</b>
<b>7</b>	XRD patterns of solid <b>1-3</b>	<b>S14</b>
<b>8</b>	XRD patterns of ethanol and benzene xerogels of <b>1</b> and of as-prepared <b>1</b>	<b>S14</b>
<b>9</b>	Optimized conformation of <b>1</b>	<b>S15</b>
<b>10</b>	Photos of the gel of <b>1</b> with CuCl <sub>2</sub> in DMSO/H <sub>2</sub> O (1 vs 1, v/v, a) and SEM image of its xerogel	<b>S15</b>
<b>11</b>	T <sub>gel</sub> experiments of <b>1</b> with different equivalents of CuCl <sub>2</sub> , CuBr <sub>2</sub> and CuSO <sub>4</sub>	<b>S16</b>
<b>12</b>	Photos of the gel of <b>3</b> with HgCl <sub>2</sub> in MeCN and fluorescent microscopic SEM images of its xerogel	<b>S16</b>
<b>13</b>	<sup>1</sup> H NMR spectral changes of <b>1-3</b> upon titration with HgCl <sub>2</sub> in THF- <i>d</i> <sub>8</sub>	<b>S17</b>
<b>14</b>	Fluorescence spectral changes of <b>1</b> -DMSO/H <sub>2</sub> O (1:1 v/v) gel upon addition of different cations	<b>S18</b>
<b>15</b>	Fluorescence spectral changes of <b>1</b> -DMSO/H <sub>2</sub> O (1:1 v/v) gel upon addition of different amounts of CuBr <sub>2</sub> and CuSO <sub>4</sub>	<b>S18</b>
<b>16</b>	Fluorescence spectral changes of <b>1</b> -DMSO/H <sub>2</sub> O (1:1 v/v) sol upon addition of different amounts of CuCl <sub>2</sub>	<b>S19</b>

## **Materials and Methods**

Unless otherwise specified, all commercial products and reagents (Alfa Aesar and Acros, respectively) were used as purchased, without further purification. All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on silica gel F254 plates. Melting points were recorded by using a KER-3100-08s heating stage with a microscope and are uncorrected.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra for all compounds were acquired in deuterated solvents (as indicated) on a Bruker Avance III 500 spectrometer. The chemical shift data are reported in units of  $\delta$  (ppm) relative to residual solvent. UV/Vis absorption spectra were measured with a Shimadzu 3600 UV–Vis–near-IR spectrophotometer and corrected for background signal with a cuvette containing the same solvent used for analysis. FT-IR spectra were measured on gels with a closed IR cell equipped with dried  $\text{CaF}_2$  windows on a Bruker Optics VERTEX 80v apparatus. For solid samples, the powder was simply deposited between two dried KBr pellets. Fluorescence spectra were measured on a FLS980 transient and steady state fluorescence spectrometer. SEM pictures were taken using a JEOL JEM-6700F scanning electron microscope with 3 kV operating voltage. TEM was performed on a JEOL JEM-2100F transmission electron microscope. Elemental analysis was carried out using a Vario micro cube elemental analyzer.

### **Gelation test**

**Organogels.** A certain weighed amount of compound was added with a measured volume of the selected solvent in test tubes. It was put under ultrasonification for a short while. Then the tube was capped and the mixture was heated in an oil bath (105 °C) for one minute. Then it was put at room temperature. The test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G), insoluble material (I), precipitations (P) or solution (S) was decided.

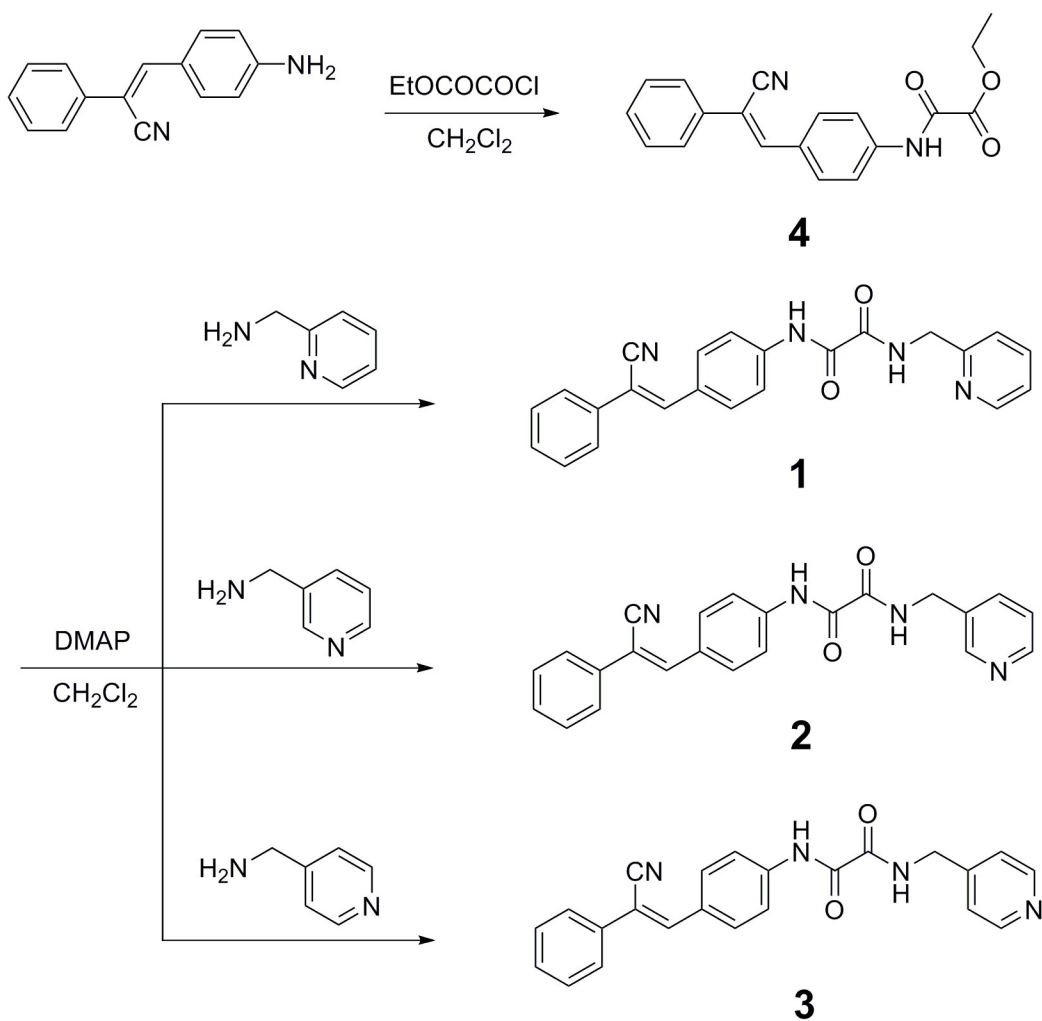
**Metallogels.** A certain amount of compound and the metal salts at different molar ratio was added in test tubes. Then a selected solvent was added and the test tube was capped. The mixture was put under ultrasonification for a short while. Then green turbid solutions (with  $\text{Cu}^{2+}$  salts) or light yellow turbid solutions (with  $\text{Hg}^{2+}$  salts) were got. The turbid solutions were heated at 105 °C for three to five minutes. All the categories were not soluble during heating. Then the hot mixtures were put at room temperature until cooled down. The test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G) was decided.

**HCl-induced Hydrogels.** A certain amount of compound was added in test tubes. Then a solvent mixture of concentrated acid with pure water (1 vs 9, v/v) was added. The test tube was capped and heated at 95 °C for two minutes. After cooling down at room temperature, the test tubes were inverted to observe whether the content of the tube could still flow or not, thus the formation of gel (G) was decided.

### **Rheology measurement**

Rheological recordings of the gels were conducted on an Anton Paar MCR302 rheometer with a plate geometry (PP 25). The distance between the plates was set to 0.2 mm. Dynamic strain sweep measurements of  $G'$  and  $G''$  were carried out with an oscillation from 0.01 to 100% (with a frequency  $\omega = 6.28 \text{ rad s}^{-1}$ ) at 25 °C. Frequency dependency experiments of  $G'$  and  $G''$  were conducted with the angular frequency between 0.01 and 100  $\text{rad s}^{-1}$  (with a strain  $\gamma = 0.1\%$ ) at 25 °C, and the frequency dependency experiments were performed in the linear viscoelastic region to ensure that the calculated parameters correspond to an intact network structure. The dynamic time sweep tests of  $G'$  and  $G''$  were carried out with a constant frequency of 6.28  $\text{rad s}^{-1}$  and different applied strains were set among different gels (**1**-benzene gel, 0.5% - 9%; **1**-DMSO/H<sub>2</sub>O (1 vs 1, v/v) gel, 3% - 50%; **1**-CuCl<sub>2</sub> gel, 5% - 70%; **3**-HgCl<sub>2</sub> gel, 0.5% - 40%).

## Synthesis of 1-3



*Synthesis of N*-[4-(2-Cyano-2-phenyl-vinyl)-phenyl]-oxalamic acid ethyl ester (**4**): Ethyl oxalyl chloride (0.57 mL, 5.32 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (5 mL) was added dropwise into a mixture of 3-(4-Amino-phenyl)-2-phenyl-acrylonitrile (0.91 g, 4.14 mmol) and triethylamine (0.74 mL, 5.32 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (40 mL) over 1 h at 0 °C, and stirred for 3 days at room temperature. The mixture was washed with water (2 x 50 mL), saturated aqueous ammonium chloride (3 x 50 mL), and water again (2 x 50 mL). The organic layer was dried over  $\text{MgSO}_4$  and evaporated. The

product was gained as light yellow solid of **4** (1.25 g, yield: 95%). M. p. = 139 °C; <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ /ppm = 9.05 (s, 1H, NH-), 7.93 (d, *J* = 8.6 Hz, 2H, ArH), 7.77 (d, *J* = 8.7 Hz, 2H, ArH), 7.67 (d, *J* = 7.5 Hz, 2H, ArH), 7.49 (s, 1H, CH-), 7.45 (t, *J* = 7.4 Hz, 2H, ArH), 7.39 (t, *J* = 7.3 Hz, 1H, ArH), 4.44 (q, *J* = 7.1 Hz, 2H, CH<sub>2</sub>-), 1.44 (t, *J* = 7.1 Hz, 3H, -CH<sub>3</sub>); <sup>13</sup>C-NMR (126 MHz, CDCl<sub>3</sub>) δ /ppm = 160.71, 153.99, 141.02, 138.10, 134.41, 130.80, 130.51, 129.18, 125.96, 119.96, 118.07, 111.13, 77.06, 76.81, 63.98, 14.02.

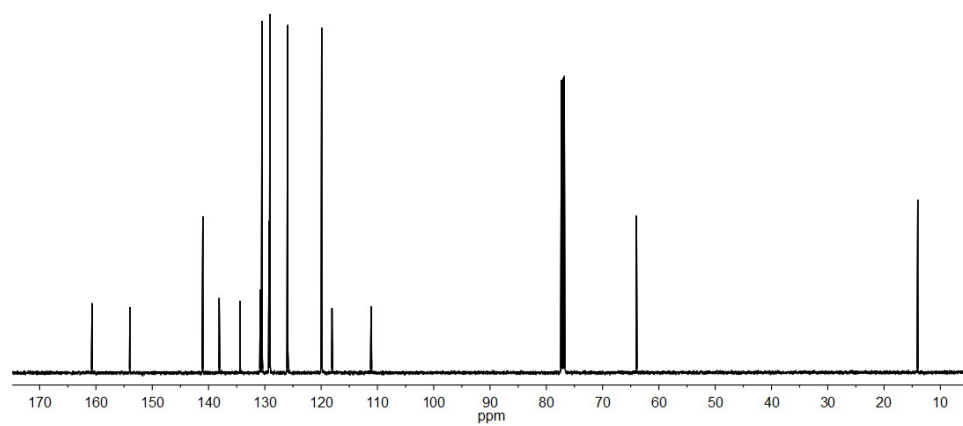
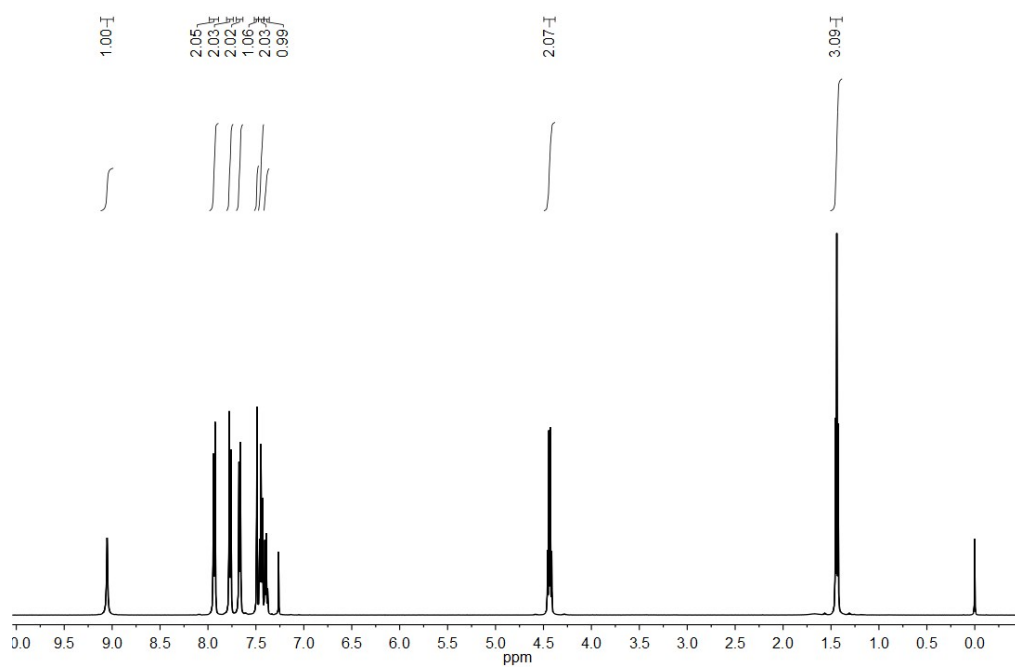
*Synthesis of 1*: 2-Pyridinemethanamine (0.48 mL, 4.68 mmol) was added to *N*-[4-(2-Cyano-2-phenyl-vinyl)-phenyl]-oxalamic acid ethyl ester (1.25 g, 3.90 mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (70 mL) and catalytically amount of DMAP (30 mg). After the mixture was stirred at room temperature for 2 days, the reaction mixture was evaporated and washed with MeOH followed by ether. **1** was obtained as white solid (1.11 g, yield: 74%). M. p. = 202 °C; FT-IR (KBr) v/cm<sup>-1</sup> = 3348, 3315, 3066, 3022, 1671, 1611, 1584, 1527, 1477, 1423, 1367; <sup>1</sup>H- NMR (500 MHz, DMSO-d<sub>6</sub>) δ /ppm = 11.00 (s, 1H, NH-), 9.57 (t, *J* = 4.9 Hz, 1H, NH-), 8.54 (d, *J* = 3.5 Hz, 1H, ArH), 8.04 (d, *J* = 7.0 Hz, 2H, ArH), 8.01 – 7.95 (m, 3H, CH- and ArH), 7.82 – 7.73 (m, 3H, ArH), 7.52 (t, *J* = 6.1 Hz, 2H, ArH), 7.45 (t, *J* = 5.8 Hz, 1H ArH), 7.36 (d, *J* = 6.3 Hz, 1H, ArH), 7.33 – 7.26 (m, 1H, ArH), 4.55 (d, *J* = 4.9 Hz, 2H, CH<sub>2</sub>-); <sup>13</sup>C-NMR (126 MHz, DMSO-d<sub>6</sub>) δ /ppm = 160.50, 159.28, 157.77, 149.36, 142.71, 140.16, 137.25, 134.39, 130.43, 130.18, 129.62, 126.14, 122.75, 121.55, 120.84, 118.61, 109.41, 44.93. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C, 72.24; H, 4.74; N, 14.65; Found: C, 72.12; H, 4.23; N, 14.47. ESI-MS m/z: calcd for [**1** + H]<sup>+</sup>, 383.4220; Found, 383.4597.

*Synthesis of 2:* 3-Pyridinemethanamine (0.27 mL, 2.62 mmol) was added to *N*-[4-(2-Cyano-2-phenyl-vinyl)-phenyl]-oxalamic acid ethyl ester (0.7 g, 2.19 mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and catalytically amount of DMAP (30 mg). After the mixture was stirred at room temperature for 2 days, the reaction mixture was evaporated and washed with MeOH followed by ether. **2** was obtained as yellow solid (0.74 g, yield: 89%). M. p. = 240 °C; FT-IR (KBr)  $\nu/\text{cm}^{-1}$  = 3332, 3274, 3091, 3042, 1667, 1592, 1558, 1515, 1449, 1419, 1360; <sup>1</sup>H-NMR (500 MHz, DMSO-d<sub>6</sub>)  $\delta$  /ppm = 10.96 (s, 1H, NH-), 9.68 (t, *J* = 5.0 Hz, 1H, NH-), 8.56 (d, *J* = 1.3 Hz, 1H, ArH), 8.48 (dd, *J* = 3.8, 1.1 Hz, 1H, ArH), 8.00 (d, *J* = 7.2 Hz, 3H, CH- and ArH), 7.95 (d, *J* = 7.1 Hz, 2H, ArH), 7.74 (dd, *J* = 8.6, 6.3 Hz, 3H, ArH), 7.52 (t, *J* = 6.1 Hz, 2H, ArH), 7.44 (t, *J* = 5.8 Hz, 1H, ArH), 7.37 (dd, *J* = 6.1, 3.9 Hz, 1H, ArH), 4.43 (d, *J* = 5.0 Hz, 2H, CH<sub>2</sub>-); <sup>13</sup>C-NMR (126 MHz, DMSO-d<sub>6</sub>)  $\delta$  /ppm = 160.52, 159.22, 149.47, 148.78, 142.71, 140.13, 135.78, 134.57, 134.38, 130.41, 130.18, 129.62, 126.14, 123.97, 120.83, 118.60, 109.40, 40.89. Anal. Calcd for C<sub>23</sub>H<sub>18</sub>N<sub>4</sub>O<sub>2</sub>: C, 72.24; H, 4.74; N, 14.65; Found: C, 71.88; H, 4.45; N, 14.68. ESI-MS *m/z*: calcd for [**2** + H]<sup>+</sup>, 383.4220; Found, 383.4547.

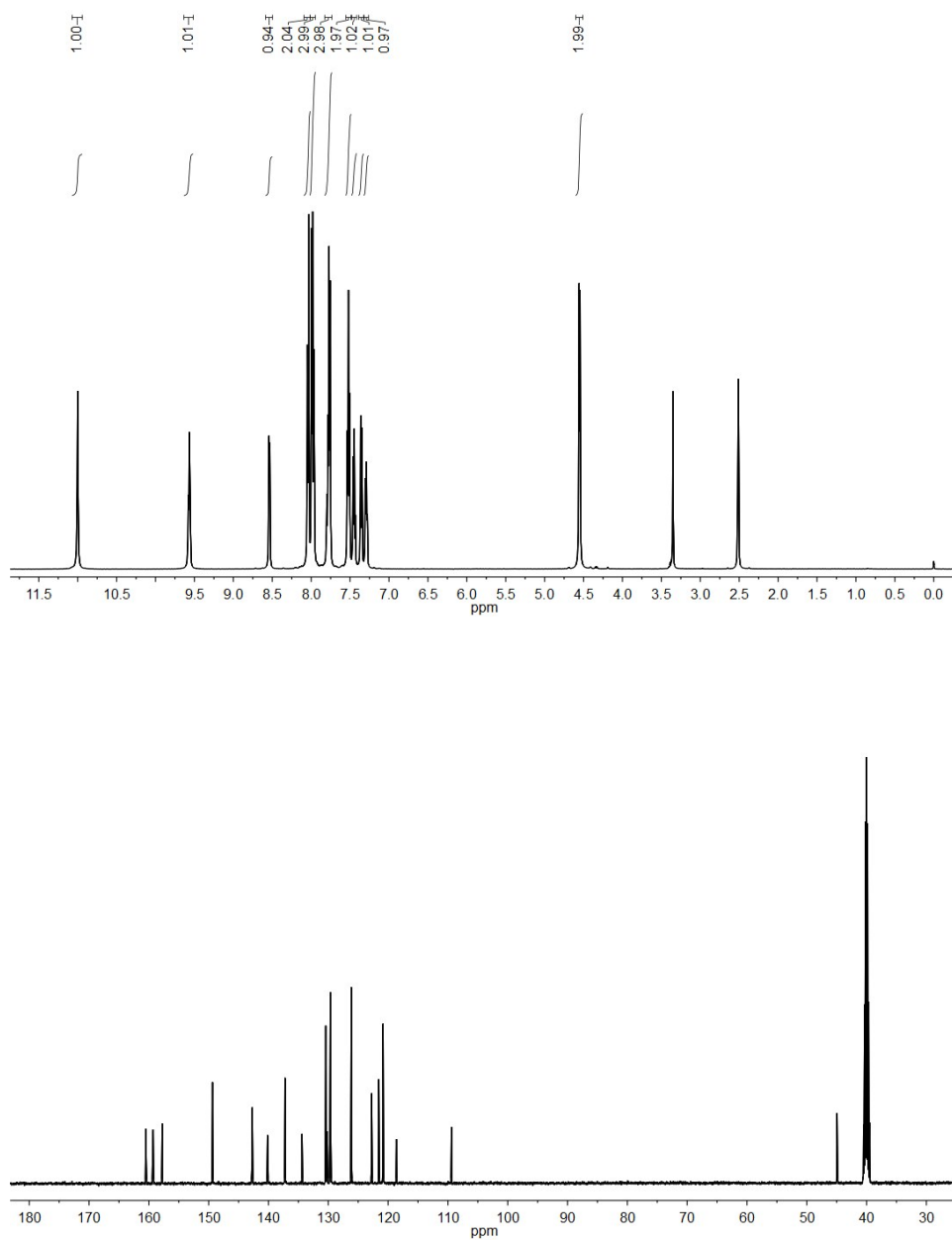
*Synthesis of 3:* 4-Pyridinemethanamine (0.27 mL, 2.62 mmol) was added to *N*-[4-(2-Cyano-2-phenyl-vinyl)-phenyl]-oxalamic acid ethyl ester (0.7 g, 2.19 mmol) dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) and catalytically amount of DMAP (30 mg). After the mixture was stirred at room temperature for 2 days, the reaction mixture was evaporated and washed with MeOH followed by ether. **3** was obtained as white solid (0.68 g, yield: 81%). M. p. = 246 °C; FT-IR (KBr)  $\nu/\text{cm}^{-1}$

= 3291, 3081, 3047, 1665, 1601, 1521, 1450, 1416, 1388, 1325;  $^1\text{H-NMR}$  (500 MHz,  $\text{DMSO-d}_6$ )  
 $\delta$  /ppm = 10.98 (s, 1H, NH-), 9.70 (t,  $J = 5.1$  Hz, 1H, NH-), 8.53 (dd,  $J = 3.6, 1.2$  Hz, 2H, ArH),  
8.05 - 8.00 (m, 3H, CH- and ArH), 7.97 (d,  $J = 7.1$  Hz, 2H, ArH), 7.79 - 7.75 (m, 2H, ArH),  
7.53 (t,  $J = 6.1$  Hz, 2H, ArH), 7.46 (t,  $J = 5.9$  Hz, 1H, ArH), 7.32 (d,  $J = 4.7$  Hz, 1H, ArH), 4.45  
(d,  $J = 5.1$  Hz, 2H,  $\text{CH}_2$ -);  $^{13}\text{C-NMR}$  (126 MHz,  $\text{DMSO-d}_6$ )  $\delta$  /ppm = 160.72, 159.16, 150.04,  
147.90, 142.72, 140.14, 134.39, 130.42, 130.20, 129.64, 126.15, 122.69, 120.85, 118.61, 109.42,  
42.23. Anal. Calcd for  $\text{C}_{23}\text{H}_{18}\text{N}_4\text{O}_2$ : C, 72.24; H, 4.74; N, 14.65; Found: C, 71.83; H, 4.34; N,  
14.46. ESI-MS  $m/z$ : calcd for  $[\mathbf{3} + \text{H}]^+$ , 383.4220; Found, 383.4530.

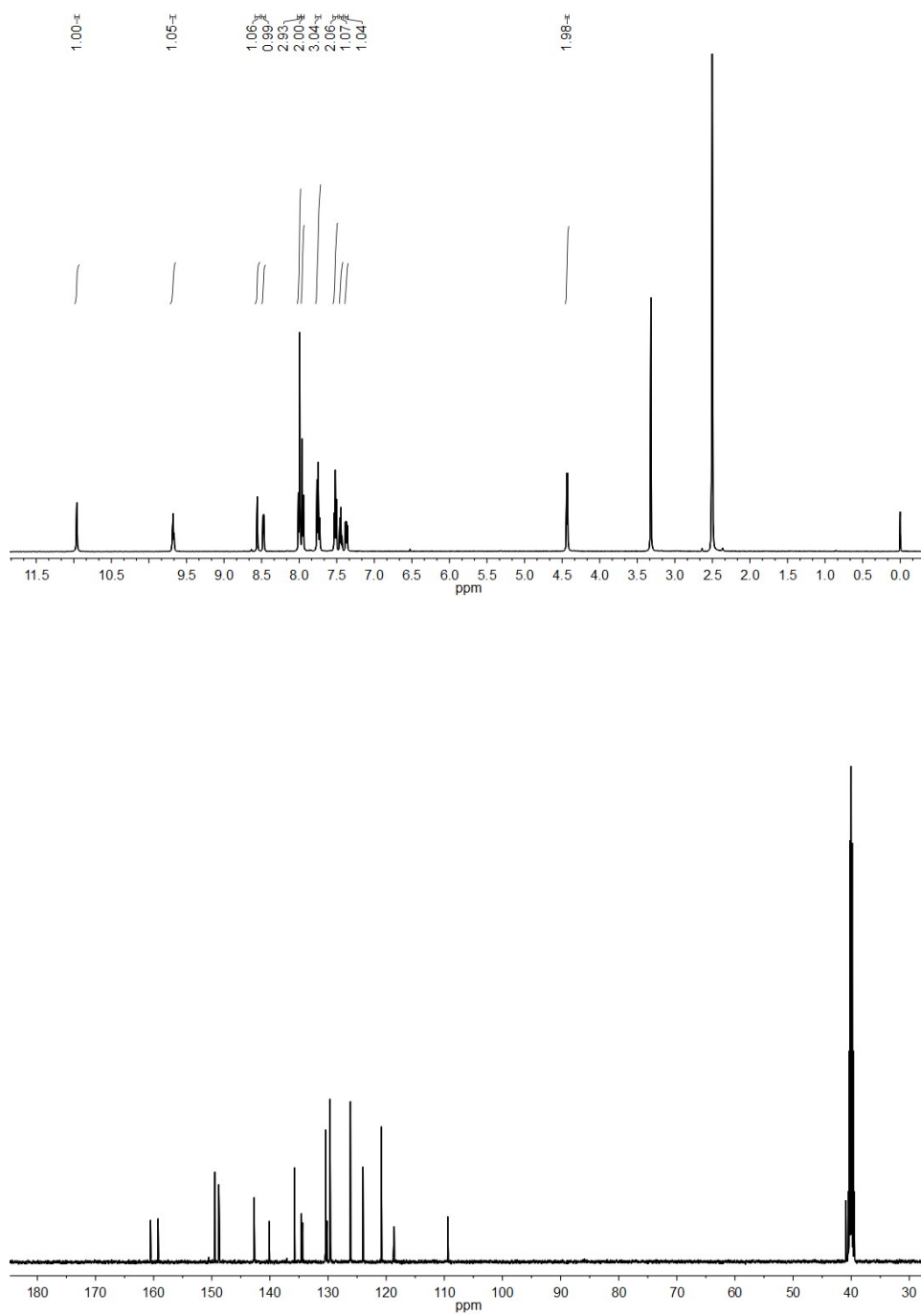




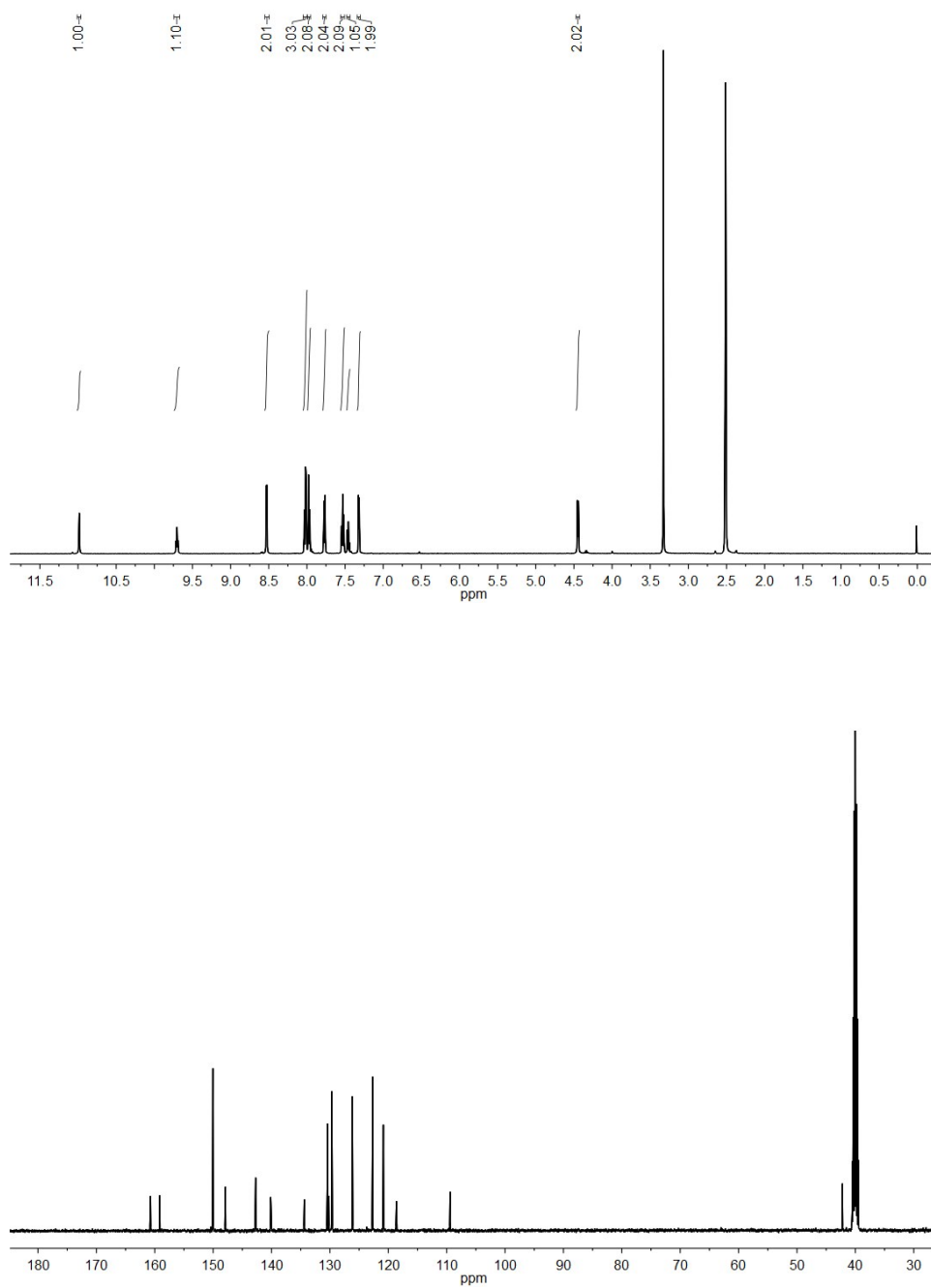
**Figure S1.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of **4**.



**Figure S2.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of **1**.



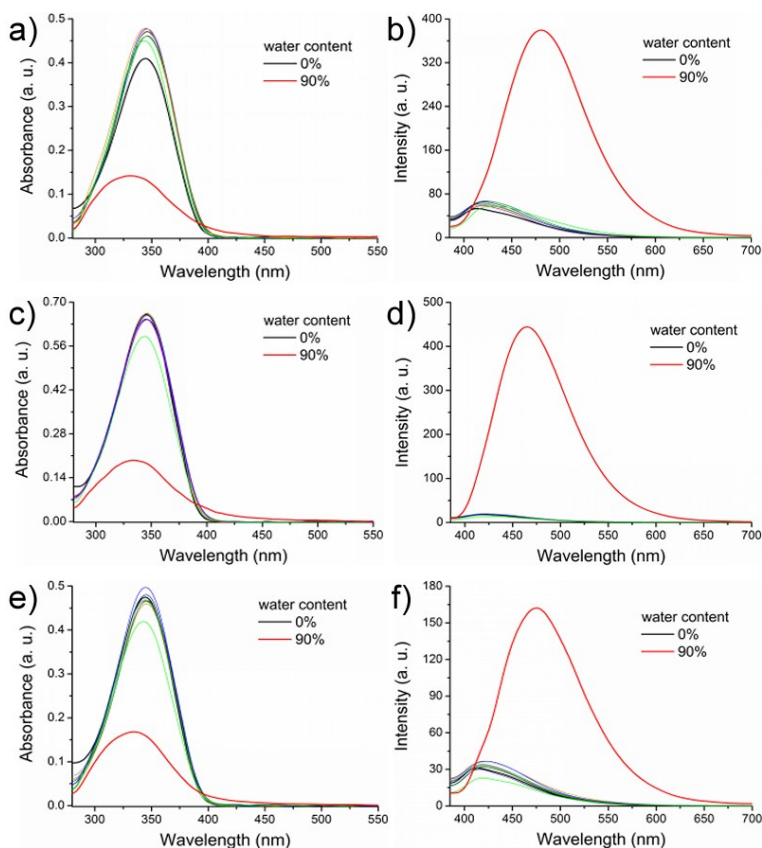
**Figure S3.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of **2**.



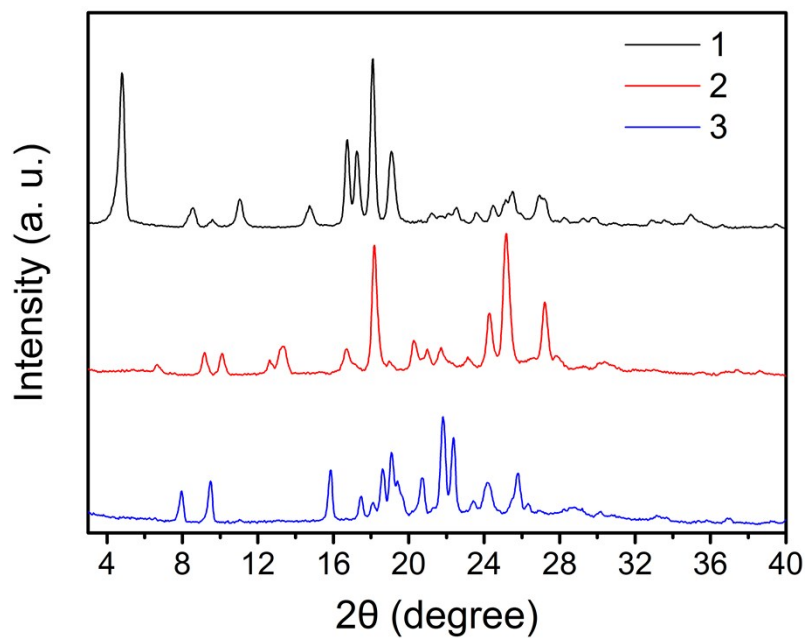
**Figure S4.**  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  spectra of **3**.

## Sample preparation for AIE measurement

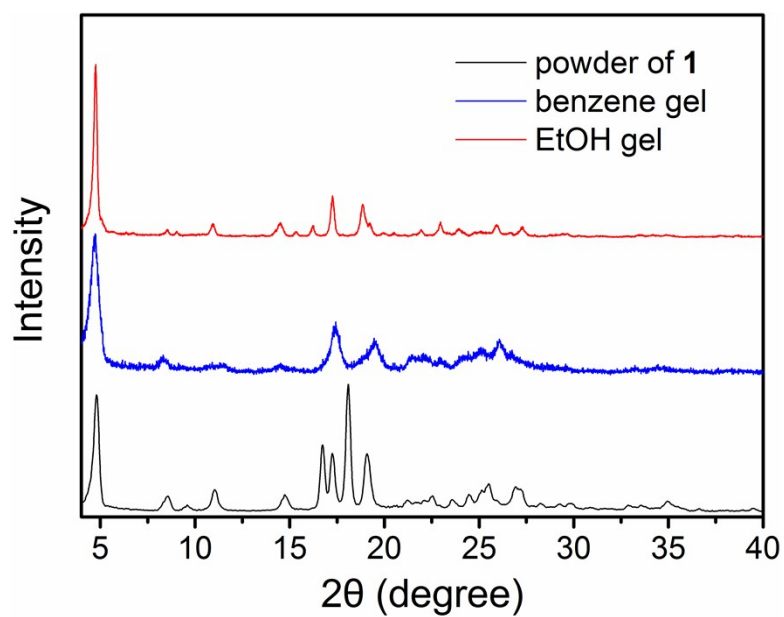
Stock THF solutions of the cyanostilbene derivatives **1-3** with a concentration of  $1 \times 10^{-4}$  M were prepared. Aliquots of the stock solution were transferred to 10 mL volumetric flasks. After appropriate amounts of THF were added, water was added dropwise under vigorous stirring to furnish  $1 \times 10^{-5}$  M solutions with different water fractions (0–90 vol%). Emission spectra of the resulting solutions or suspensions were then recorded immediately.



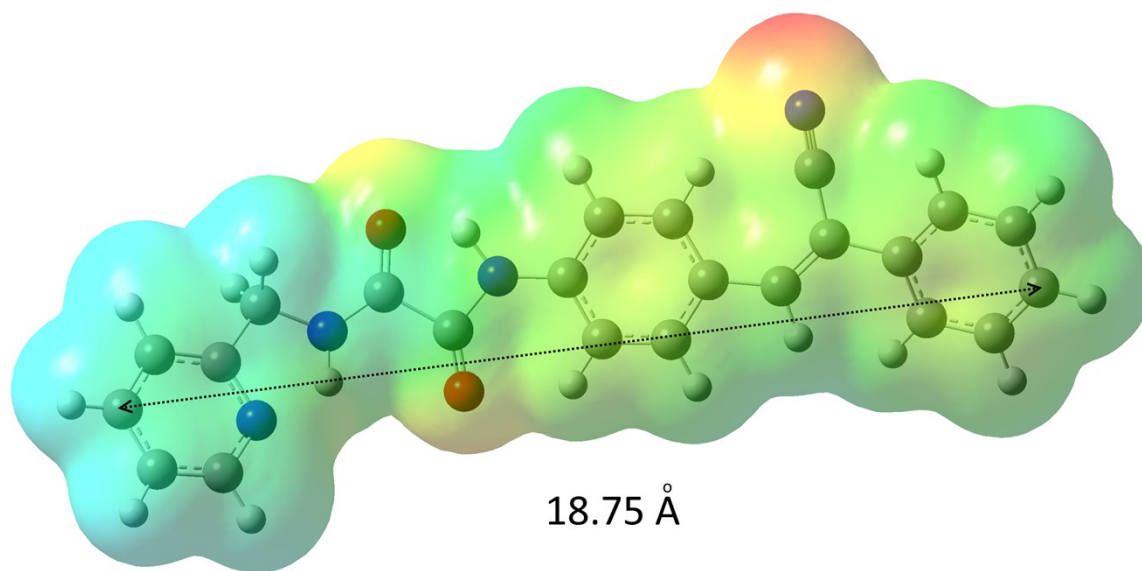
**Figure S5.** UV absorption spectra of a) **1**; c) **2**; e) **3** in THF/water mixture solvents with different volume ratio (concentration:  $10^{-5}$  M, water fraction: from 0% to 90%). b), d) and f) Fluorescent spectra of the corresponding solutions of **1-3** in THF/water.



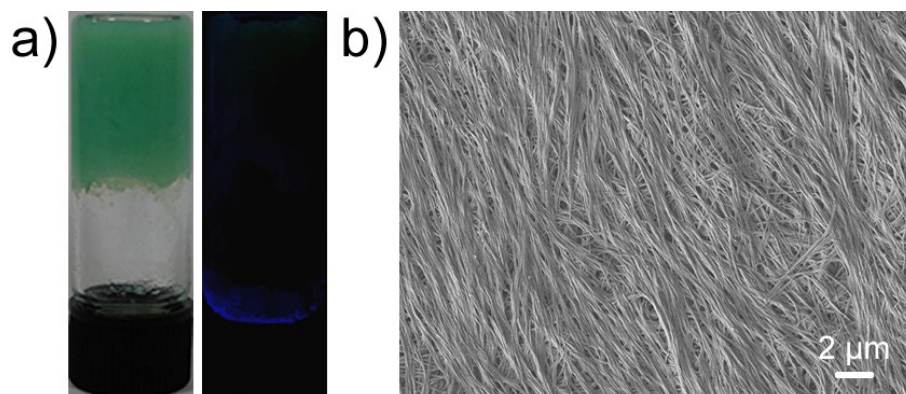
**Figure S6.** XRD patterns of solid **1** – **3**.



**Figure S7.** XRD patterns of ethanol and benzene xerogels of **1** and of as-prepared **1**.



**Figure S8.** Optimized conformation of **1** obtained from DFT calculations at the B3LYP/6-31G(d) level.

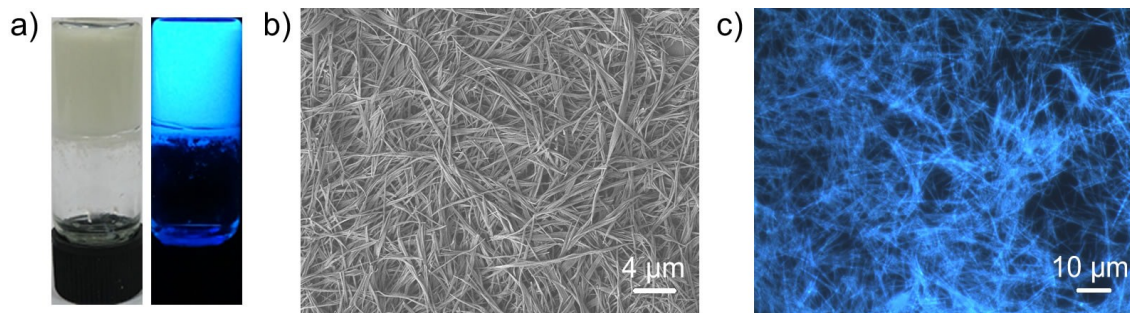


**Figure S9.** Photos of the gel of **1** with  $\text{CuCl}_2$  (1:1 in molecular ratio) in DMSO/ $\text{H}_2\text{O}$  (1 vs 1, v/v, a) and SEM image of its xerogel (b).

**Table S1**  $T_{\text{gel}}$  experiments of **1** with different equivalents of  $\text{CuCl}_2$ ,  $\text{CuBr}_2$  and  $\text{CuSO}_4$  in  $\text{DMSO}/\text{H}_2\text{O}$  (1:1 v/v).<sup>[a]</sup>

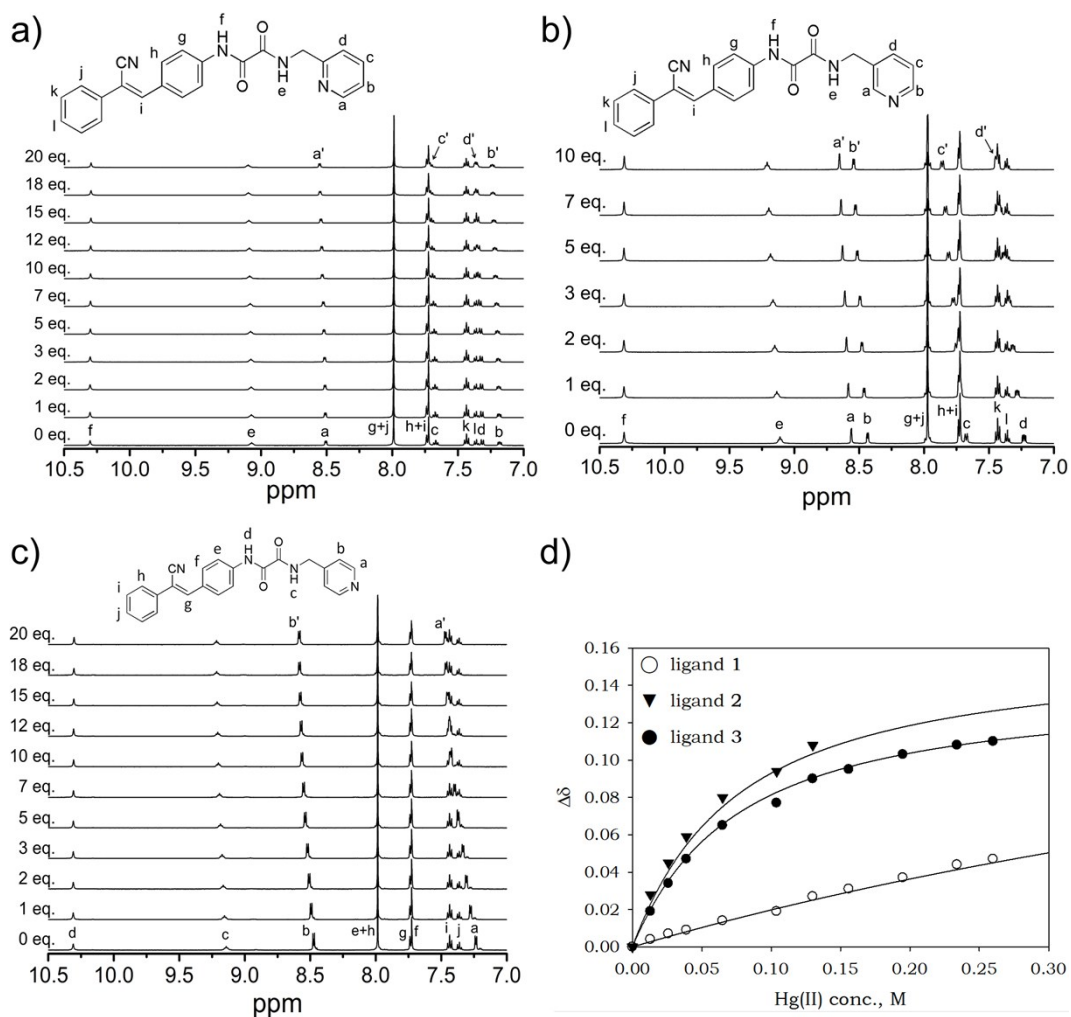
ligand : metal ratio	$\text{CuCl}_2$	$\text{CuBr}_2$	$\text{CuSO}_4$
<b>1 : 0</b>	G (65 °C)	G (65 °C)	G (65 °C)
<b>4 : 1</b>	G (69 °C)	WG (-)	P (-)
<b>2 : 1</b>	G (84 °C)	P (-)	G (75 °C)
<b>1 : 1</b>	G (95 °C)	G (97 °C)	G (88 °C)
<b>1 : 2</b>	G (77 °C)	G (86 °C)	G (71 °C)
<b>1 : 4</b>	G (72 °C)	G (74 °C)	G (69 °C)

<sup>[a]</sup> Concentration of **1** is  $10 \text{ mg mL}^{-1}$ . The ratio of **1** vs metal salt is in molar ratio. G: gel; WG: weak gel; P: precipitations.

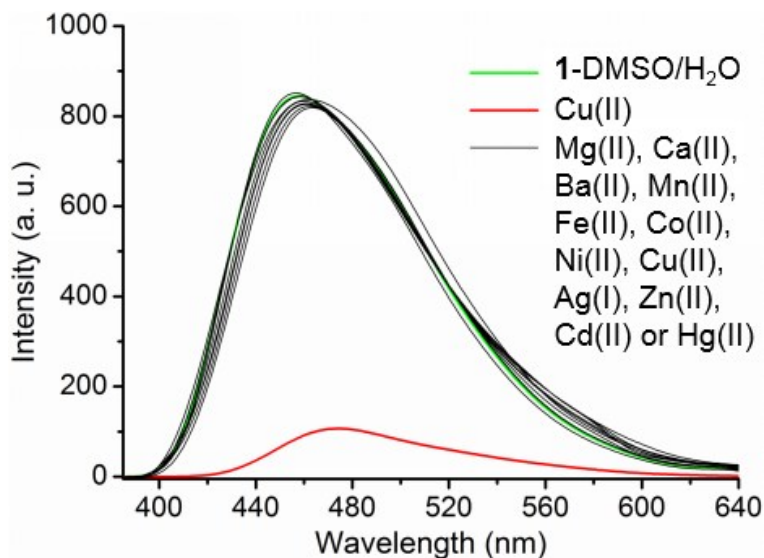


**Figure S10.** Photos of the gel of **3** with  $\text{HgCl}_2$  (1:1 ratio) in MeCN (a); fluorescent microscopic (b) and SEM (c) images of its xerogel.

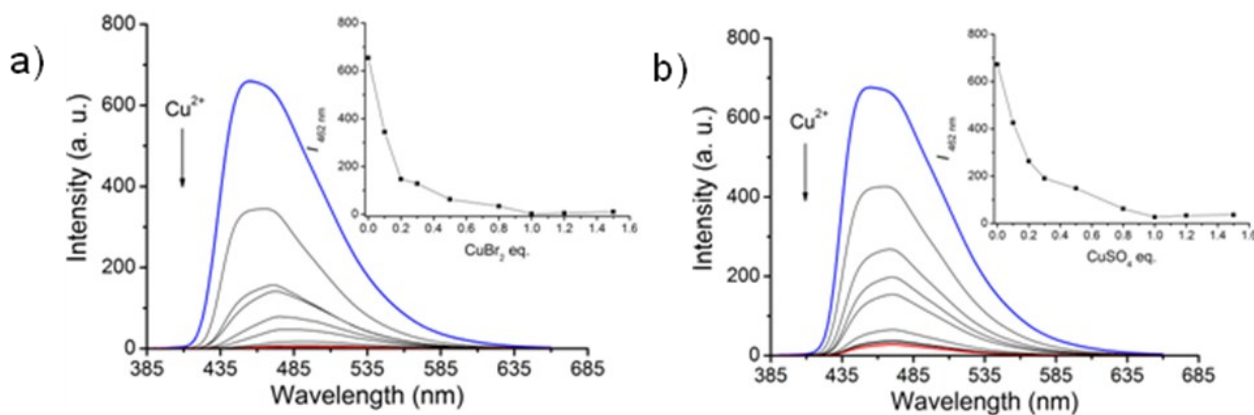




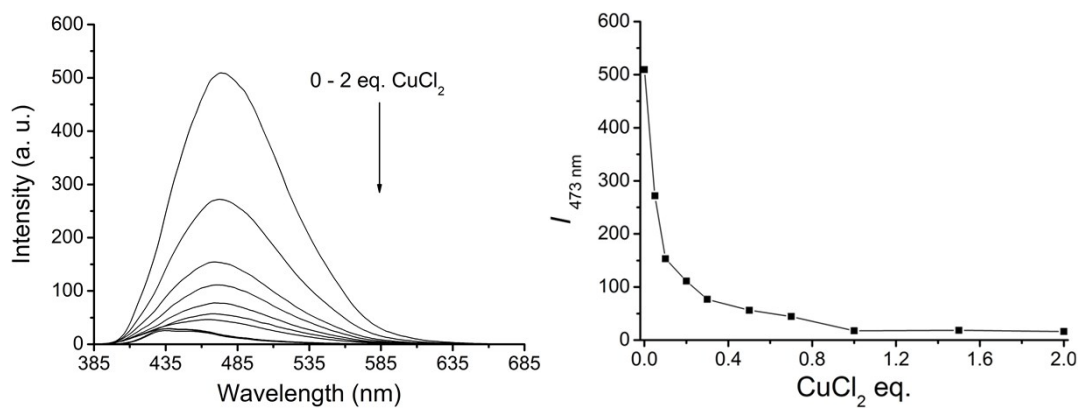
**Figure S11.** <sup>1</sup>H-NMR spectra (a-c) of **1-3** in THF-*d*<sub>8</sub> (1.3 × 10<sup>-3</sup> M) upon addition of increasing amounts of HgCl<sub>2</sub> at 300 K and d) plot of the chemical shift variations of ligands **1-3** vs. HgCl<sub>2</sub> concentration ( $H_a$  for ligands **1** and **2** and  $H_b$  for ligand **3**, respectively). Lines represent best fit curves.



**Figure S12.** Fluorescence spectra of **1**-DMSO/H<sub>2</sub>O (1:1 v/v) gel (10 mg mL<sup>-1</sup>) with addition of different cations using their chloride salts as the sources, **1** : cation = 1 : 5 ( $\lambda_{\text{ex}} = 365$  nm).



**Figure S13.** Fluorescent spectra of **1**-DMSO/H<sub>2</sub>O gels (10 mg mL<sup>-1</sup>) with increasing concentrations of CuBr<sub>2</sub> and CuSO<sub>4</sub>, respectively (from 0 to 1.5 equivalents); inset: plot of the normalized fluorescence intensity at 462 nm vs different concentrations of copper salts.



**Figure S14.** Fluorescence spectra of **1**-DMSO/H<sub>2</sub>O (1:1 v/v) sol (10<sup>-3</sup> M) upon addition of different amounts of CuCl<sub>2</sub> ( $\lambda_{\text{ex}} = 365$  nm).