Supporting Information

Bromide anion-triggered visible responsive metallogels based on squaramide complexes

Di Wu,* Ruyong Jiang, Liang Luo, Zhen He, and Jingsong You*

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I. General remarks

High-resolution mass spectra (HRMS) were obtained by a Waters-Q-TOF-Premier (ESI+). Melting points (M.p.) were determined with XRC-1 without correction.

TBAF: tetrabutylammonium fluoride; TBAC: tetrabutylammonium chloride; TBAB: tetrabutylammonium bromide; TBAI: tetrabutylammonium iodide.

II. Gelation tests, structure and spectra

![Figure S1](image1). Optimization of gelator composition. Molar ratios of \( L^4/CuCl_2\cdot2H_2O \) are marked in the photos.

![Figure S2](image2). Optimization of the gelator concentration in MeOH. The weight concentration (wt%) of the gelator \( L^4/CuCl_2\cdot2H_2O \) (molar ratio = 1:1) are marked in the photos.

<table>
<thead>
<tr>
<th>Table S1</th>
<th>Gelation behavior of ( L^4/CuCl_2\cdot2H_2O ) (molar ratio = 1:1) in different solvents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry</td>
<td>Solvent (( v:v ) if applicable)</td>
</tr>
<tr>
<td>1</td>
<td>MeOH</td>
</tr>
<tr>
<td>2</td>
<td>H(_2)O</td>
</tr>
<tr>
<td>3</td>
<td>DMF</td>
</tr>
<tr>
<td>4</td>
<td>DMSO</td>
</tr>
<tr>
<td>5</td>
<td>DMAc</td>
</tr>
<tr>
<td>6</td>
<td>MeOH/H(_2)O (1:0.1)</td>
</tr>
<tr>
<td>7</td>
<td>MeOH/H(_2)O (1:0.2)</td>
</tr>
<tr>
<td>8</td>
<td>MeOH/H(_2)O (1:0.3)</td>
</tr>
<tr>
<td>9</td>
<td>MeOH/H(_2)O (1:0.4)</td>
</tr>
</tbody>
</table>
a S: solution; G: steady gel; Gp: partial gel; P: precipitate.

**Figure S3** The packing structure of [Cu-L4]Cl2 in crystals viewed along c-axis (top) with enlarged details (bottom).
Figure S4 The packing structure of [Cu-L4]Cl2 in crystals viewed along b-axis.

Figure S5 Measured PXRD patterns of Gel-Br xerogel (bottom) in comparison with the simulated single crystal XRD [Cu-L4]Br2. Three peaks are marked with stars.
**Figure S6** The packing structure of [Cu-L4]Br2 in crystals viewed along \( a \)-axis (top) with enlarged details (bottom).
Figure S7 The packing structure of [Cu-L4]Br2 in crystals viewed along b-axis, rotated by 20° along a-axis.
**Figure S8.** (a) Samples of Gel-Cl upon addition of aqueous sodium salts (2.4 mol/L, 70 μL), aqueous bromide salts (2.4 mol/L, 70 μL) and bromide powders (10.0 equiv). For the samples upon the addition of aqueous sodium salts, photos were taken at 4 hours. (b) Raman and (d) DR-UV-vis spectra of Gel-Br and Gel-Cl before and after adding NaBr. Gel-Cl and Gel-Br gel samples were subject to Raman and DR-UV-vis spectroscopy directly. The sample of Gel-Cl + Br⁻ was prepared by mixing solid NaBr (10 equiv relative to Cl species in Gel-Cl) with Gel-Cl and placed overnight for Raman measurement. 0.2, 0.7, 1.3, 2.5, 5.0 and 10.0 equiv of solid NaBr (relative to Cl species in Gel-Cl) were mixed, respectively, with Gel-Cl and placed overnight for DR-UV-vis test. (c) Schematic representation of anion ligand exchange. Blue: N; green: Cl; purple: Br.

**Figure S9**. 30 seconds (1st row), 2 h (2nd row) and 4 h (3rd row) after Gel-Cl was exposed to 10, 5.0, 2.5, 1.3, 0.60, 0.30 and 0.0 equiv (from left to right) of NaBr in H₂O (70 μL, 4.8, 2.4, 1.2, 0.60, 0.30, 0.15 and 0.0 mol/L, respectively).
Figure S10 30 seconds (1<sup>st</sup> row), 4 h (2<sup>nd</sup> row) and 5 days (3<sup>rd</sup> row) after Gel-Cl was exposed to 5.0, 2.5, 1.3, 0.60, 0.30, 0.15 and 0.075 equiv (from left to right) of NaBr in MeOH (80 μL, 4.2, 2.1, 1.0, 0.50, 0.25, 0.13 and 0.065 mol/L, respectively).

Figure S11 Gel-Cl was exposed to tetrabutylammonium (TBAX) salt powder. Species of X<sup>-</sup> and equivalents of X<sup>-</sup> were marked in the photos.

Figure S12 Samples of Gel-Cl with KBr, NaBr, BEAB, TEAB, TOAB, HTMAB, DMIMB, EPIMB, PDIMB and MTPB solid (10.0 equiv) upon addition of TBAC after 90 days (10.0 equiv, from left to right).
Figure S13 Transformations of Gel-Cl upon adding an aqueous NaBr solution (70 μL, 4.8 mol/L).

III. Calculations

The density functional theory (DFT)/B3LYP calculation were performed using Gaussian 09 package. The crystal structures obtained from the SXRD were used for the single point calculations with a Lanl2DZ basis set on Cu and 6-31G** basis set on the rest of the atoms (C, N, O, H, Cl, Br).

Figure S14 Energy level (eV) and lobes of the front obitals of the complex [Cu-L4]Cl2.
Figure S15 Energy level (eV) and lobes of the front orbitals of the complex [Cu-L4]Br2.

References

III. Copies of $^1$H and $^{13}$C NMR spectra

$^1$H NMR spectrum of 2-($^{1}H$-imidazol-1-yl)ethanamine in CDCl$_3$

$^{13}$C NMR spectrum of 2-($^{1}H$-imidazol-1-yl)ethanamine in CDCl$_3$
$^1$H NMR spectrum of L4 in DMSO-$d_6$

$^{13}$C NMR spectrum of L4 in DMSO-$d_6$

$^1$H NMR spectrum of L5 in DMSO-$d_6$
$^{13}$C NMR spectrum of L5 in DMSO-$d_6$