

Supporting Information For

High iodine-species enriching and guest-driven tunable luminescent properties based on a cadmium(II)-triazole MOF

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Experimental Section

2: Single crystals of **1** exposed to iodine vapor in a sealed jar containing iodine crystals for 48 h at room temperature to generate **2**. IR (KBr pellet cm^{-1}): 3548 (w), 1607 (s), 1485 (s), 1402 (ms), 1090 (s), 1010 (ms), 797 (s), 692 (ms), 624 (s). Elemental analysis(%) calcd for $\text{C}_{48}\text{H}_{36}\text{CdCl}_2\text{I}_4\text{N}_{12}\text{O}_8$ (**2**): C 36.04, H 2.27, N 10.51; found: C 36.23, H 2.37, N 10.12.

3: Crystals of **1** were immersed in a hexane solution of I_2 (0.02mol/L) for 2 h, 6 h and 20 h to generate **3**, **3'** and **3''**. IR (KBr pellet cm^{-1}): 3541 (w), 1608(s), 1522 (w), 1485 (ms), 1403 (ms), 1091 (s), 1011 (ms), 797(s), 692 (ms), 624 (s). Elemental analysis(%) calcd for: $\text{C}_{48}\text{H}_{36}\text{CdCl}_2\text{I}_{0.80}\text{N}_{12}\text{O}_8$ (**3**): C 48.30, H 3.04, N 14.08; found: C 48.07, H 2.92, N 13.88. $\text{C}_{48}\text{H}_{36}\text{CdCl}_2\text{I}_{1.40}\text{N}_{12}\text{O}_8$ (**3'**): C 45.40, H 2.86, N 13.24; found: C 45.14, H 2.75, N 13.05. $\text{C}_{48}\text{H}_{36}\text{CdCl}_2\text{I}_{1.60}\text{N}_{12}\text{O}_8$ (**3''**): C 44.51, H 2.80, N 12.98; found: C 44.35, H 2.69, N 12.84.

4-4'': Crystals of **1** were immersed in an aqueous solution of I_2/KI at 400, 40 and 0.04 ppm for 72 h to generate **4**, **4'** and **4''**, respectively. IR (KBr pellet cm^{-1}): **4**: 3534 (w), 1601(s), 1548 (w), 1481 (ms), 1400 (ms), 1093 (s), 1007 (ms), 798(s), 694 (ms), 619 (s); **4'**: 3542 (w), 1610(s), 1524 (w), 1483 (ms), 1406 (ms), 1096 (s), 1011 (ms), 798(s), 694 (ms), 623 (s); **4''**: 3533 (w), 1609(s), 1522 (w), 1483 (ms), 1404 (ms), 1099 (s), 1011 (ms), 797(s), 694 (ms), 623 (s). Elemental analysis (%) calcd for:

$C_{48}H_{36}CdCl_{1.50}I_{1.50}N_{12}O_6$ (**4**): C 46.76, H 2.94, N 13.63; found: C 46.35, H 2.72, N 13.28.

$C_{48}H_{36}CdCl_{1.7}I_{0.9}N_{12}O_{6.8}$ (**4'**): C 49.00, H 3.08, N 14.29; found: C 48.61, H 2.90, N 13.99.

$C_{48}H_{36}CdCl_{1.92}N_{12}O_{7.68}I_{0.24}$ (**4''**): C 51.72, H 3.26, N 15.08; found: C 51.35, H 3.01, N 14.79.

5-5': Crystals of **1** were stirred in an aqueous solution of $NaIO_3$ (40 ppm) for 2 and 4h to generate **5** and **5'**, respectively. IR (KBr pellet cm^{-1}): **5**: 3356 (w), 1607(s), 1551 (w), 1526 (w), 1485 (ms), 1404 (ms), 1094 (s), 1010 (ms), 797(s), 725 (ms), 690 (ms), 623 (s); **5'**: 3355 (w), 1609 (s), 1550 (w), 1526 (w), 1481 (ms), 1404 (ms), 1096 (s), 1011 (ms), 797(s), 723 (ms), 696 (ms), 623 (s). Elemental analysis(%) calcd for: $C_{48}H_{38}CdCl_{1.5}I_{0.5}N_{12}O_{8.5}$ (**5**): C 50.22 H 3.34 N 14.64; found: C 50.37, H 3.45, N 14.38; $C_{48}H_{38}CdCl_{1.2}I_{0.8}N_{12}O_{8.2}$ (**5'**): C 50.22 H 3.34 N 14.64; found: C 49.32, H 3.37, N 13.98.

Crystal data of **2**: $C_{48}H_{36}CdCl_2I_4N_{12}O_8$, $M_r = 1599.79$, tetragonal, space group $P4(1)2(1)2$, $a = 15.8346(14)$ Å, $b = 15.8346(14)$ Å, $c = 21.463(4)$ Å, $V = 5381.4(12)$ Å³, $Z = 4$, $\rho_{calcd} = 1.975$ Mg m⁻³, $\mu = 2.864$ mm⁻¹, $F(000) = 3064$, A total of 28124 reflections collected, 5010 independent reflections ($R_{int} = 0.0446$) with 4782 [$I > 2\delta(I)$] observed data, 397 parameters, $R_1 = 0.0758$, $wR_2 = 0.1789$ [$I > 2\delta(I)$] and $R_1 = 0.0790$, $wR_2 = 0.1809$ (all data) with $S = 1.147$. Crystal data of **3**: $C_{48}H_{36}CdCl_2I_{0.80}N_{12}O_8$, $M_r = 1193.71$, tetragonal, space group $P4(3)2(1)2$, $a = 15.8746(9)$ Å, $b = 15.8746(9)$ Å, $c = 21.497(2)$ Å, $V = 5417.3(7)$ Å³, $Z = 4$, $\rho_{calcd} = 1.464$ Mg m⁻³, $\mu = 1.018$ mm⁻¹, $F(000) = 2386$, A total of 28294 reflections collected, 5048 independent reflections ($R_{int} = 0.0358$) with 4854 [$I > 2\delta(I)$] observed data, 358 parameters, $R_1 = 0.0514$, $wR_2 = 0.1607$ [$I > 2\delta(I)$] and $R_1 = 0.0531$, $wR_2 = 0.1624$ (all data) with $S = 1.151$. Crystal data of **3'**: $C_{48}H_{36}CdCl_2I_{1.40}N_{12}O_8$, $M_r = 1269.85$, tetragonal, space group $P4(3)2(1)2$, $a = 15.8763(14)$ Å, $b = 15.8763(14)$ Å, $c = 21.507(4)$ Å, $V = 5421.1(12)$ Å³, $Z = 4$, $\rho_{calcd} = 1.556$ Mg m⁻³, $\mu = 1.360$ mm⁻¹, $F(000) = 2513$, A total of 28083 reflections collected, 5057 independent reflections ($R_{int} = 0.0353$) with 4861 [$I > 2\delta(I)$] observed data, 358 parameters, $R_1 = 0.0584$, $wR_2 = 0.1765$ [$I > 2\delta(I)$] and

$R_1 = 0.0601$, $wR_2 = 0.1787$ (all data) with $S = 1.156$. Crystal data of **3**^{II}: $C_{48}H_{36}CdCl_2I_{1.60}N_{12}O_8$, $Mr = 1295.23$, tetragonal, space group $P4(3)2(1)2$, $a = 15.8774(10)$ Å, $b = 15.8774(10)$ Å, $c = 21.542(3)$ Å, $V = 5430.6(8)$ Å³, $Z = 4$, $\rho_{calcd} = 1.584$ Mg m⁻³, $\mu = 1.471$ mm⁻¹, $F(000) = 2555$, A total of 28535 reflections collected, 5064 independent reflections ($R_{int} = 0.0312$) with 4885 [$I > 2\delta(I)$] observed data, 358 parameters, $R_1 = 0.0605$, $wR_2 = 0.1793$ [$I > 2\delta(I)$] and $R_1 = 0.0622$, $wR_2 = 0.1810$ (all data) with $S = 1.113$. Crystal data of **4**: $C_{48}H_{36}CdCl_{1.50}I_{1.50}N_{12}O_6$, $Mr = 1232.81$, tetragonal, space group $P4(1)2(1)2$, $a = 15.9506(19)$ Å, $b = 15.9506(19)$ Å, $c = 21.125(5)$ Å, $V = 5374.7(16)$ Å³, $Z = 4$, $\rho_{calcd} = 1.524$ Mg m⁻³, $\mu = 1.399$ mm⁻¹, $F(000) = 2436$, A total of 27043 reflections collected, 4997 independent reflections ($R_{int} = 0.0729$) with 4476 [$I > 2\delta(I)$] observed data, 349 parameters, $R_1 = 0.1046$, $wR_2 = 0.3021$ [$I > 2\delta(I)$] and $R_1 = 0.1130$, $wR_2 = 0.3081$ (all data) with $S = 1.170$. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC 808128, 808129, 808130, 808131 and 808132. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

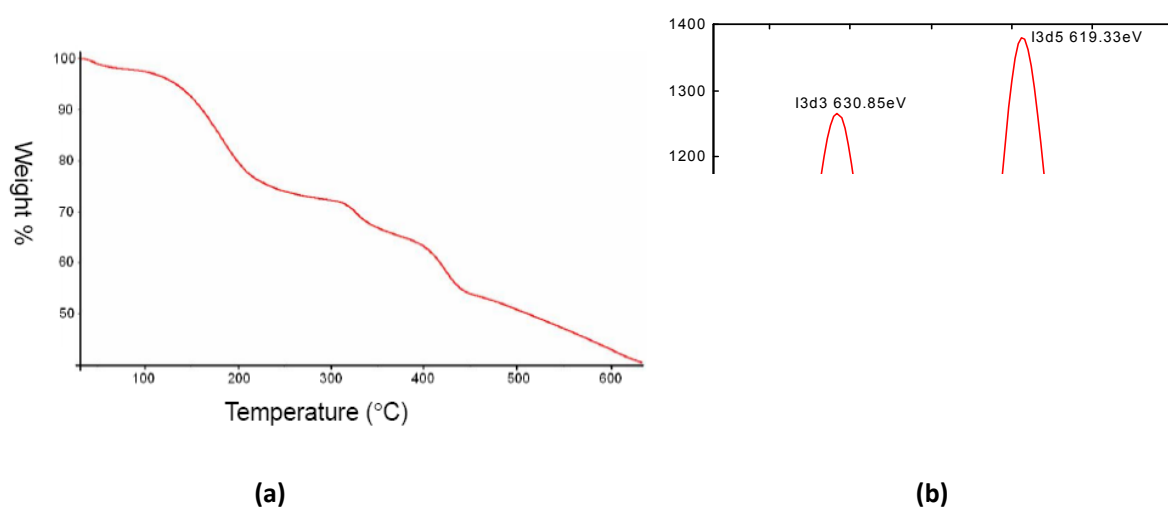


Figure S1. (a) TGA trace of **2**. The calculated and observed mass loss of iodine is 31.7 and 30.4 %, respectively. (b) XPS spectrum of **2**.

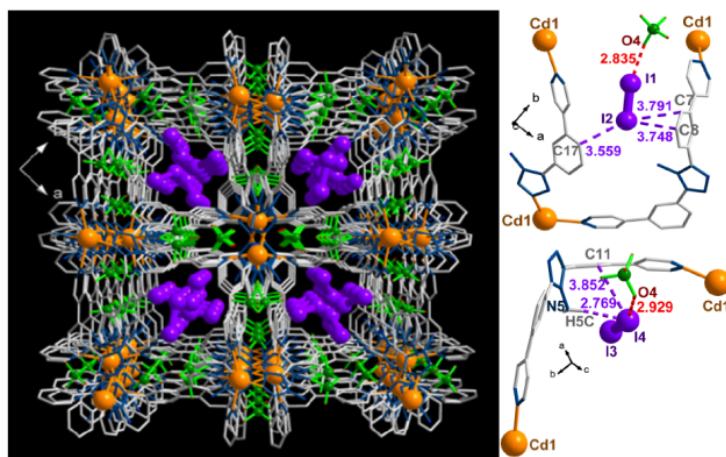


Figure S2. Upon close inspection of the structure, we found that one of the two encapsulated I_2 (I(1)-I(2)) guests is stabilized in the channels through a $ClO_4 \cdots I_2$ ($d_{I(1) \cdots O(4)} = 2.835 \text{ \AA}$) and $\pi \cdots I$ ($d_{I(2) \cdots C(7)} = 3.791$, $d_{I(2) \cdots C(8)} = 3.748$ and $d_{I(2) \cdots C(17)} = 3.559 \text{ \AA}$) interactions, while the other I_2 (I(3)-I(4)) molecule is fixed by $ClO_4 \cdots I_2$ ($d_{I(4) \cdots O(4)} = 2.929 \text{ \AA}$), $\pi \cdots I$ ($d_{I(4) \cdots C(11)} = 3.852 \text{ \AA}$) and $N-H \cdots I$ ($d_{I(4) \cdots H(5C)} = 2.769$, $d_{I(4) \cdots N(5)} = 3.643$ and $\angle N(5)-H(5C) \cdots I(4) = 140^\circ$) interactions.

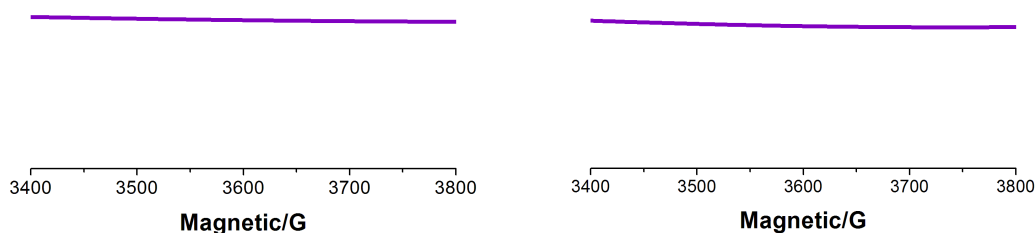


Figure S3. ESR spectra of **2** under ambient light (left) and UV light (355 nm, right), indicating no photoinduced radical species formed.

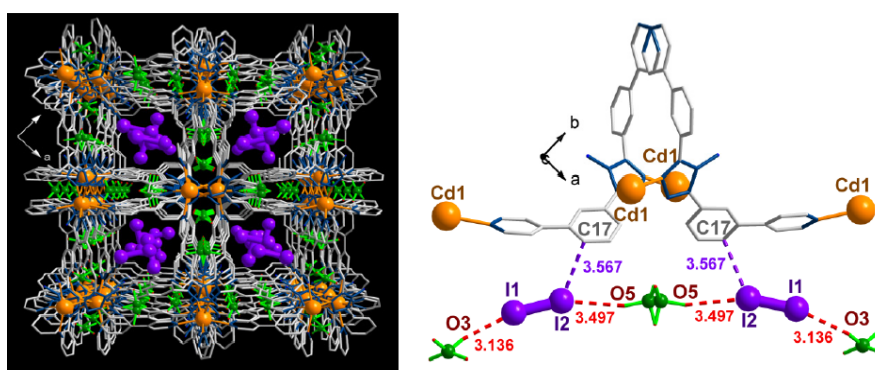


Figure S4. Single crystal structure of **3''**. Single-crystal analysis indicates that the encapsulated I_2 molecules are disordered in the cavities, so only major disordered components are shown in the figure. The $I \cdots OCl_4^-$ halogen bonding distances in **3''** are 3.316 (I(1) \cdots O(3)) and 3.497 (I(2) \cdots O(5)) \AA , respectively. In addition, I(2) atom is still π -bonded to the framework through $\pi \cdots I$ interaction with a atom-to-atom contact at 3.567 \AA

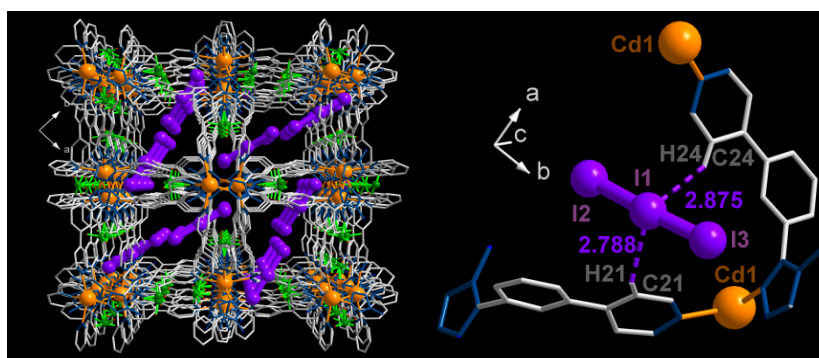


Figure S5. Single-crystal analysis of **4** indicates that the encapsulated I_3^- anions are disordered in the cavities, so only major disordered components are shown in the figure. I_3^- is hydrogen bonded to the framework through C-H...I linkages ($d_{I(1)\dots H(24)} = 2.875$, $d_{I(4)\dots C(24)} = 3.667$ and $\angle C(24)-H(24)\dots I(1) = 141^\circ$; $d_{I(1)\dots H(21)} = 2.778$, $d_{I(1)\dots C(21)} = 3.493$ and $\angle C(21)-H(21)\dots I(1) = 131^\circ$).

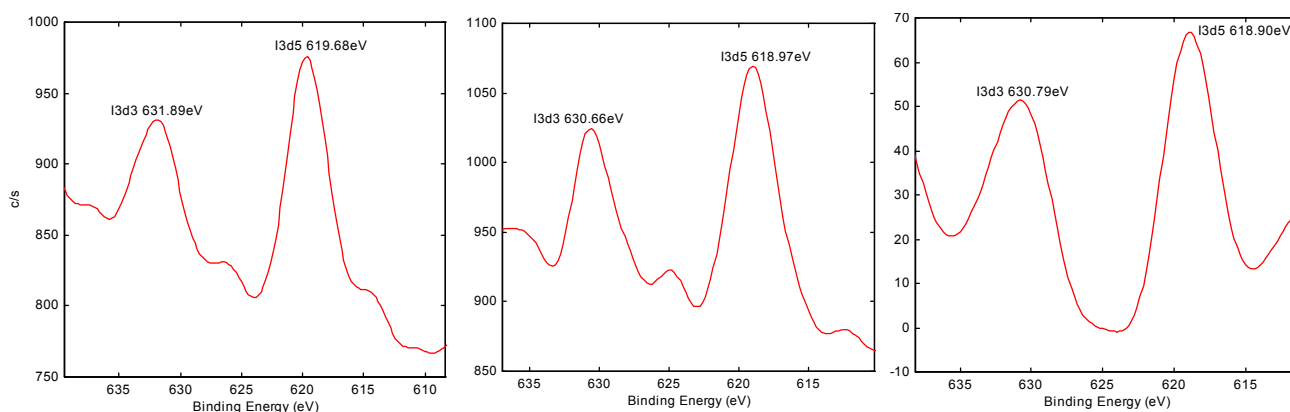


Figure S6. XPS spectra of **4** (left), **4'** (middle) and **4''** (right).

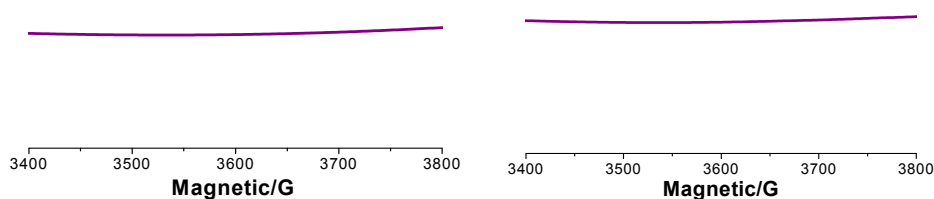


Figure S7. ESR spectra of **4** under ambient light (left) and UV light (355 nm, right), indicating no photoinduced radical species formed.

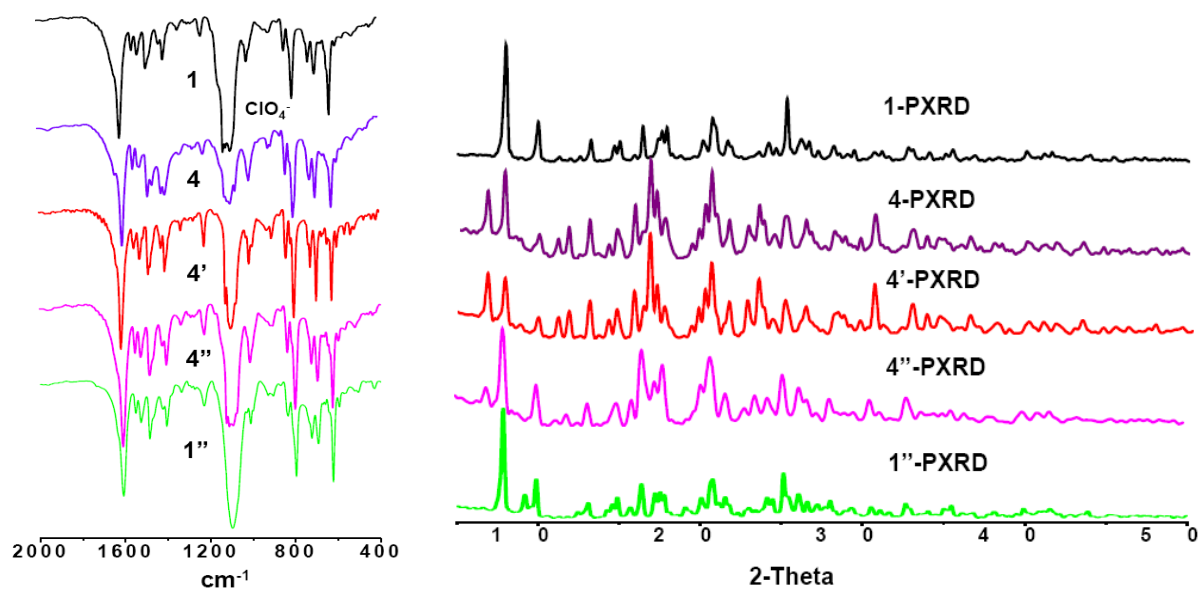


Figure S8. IR spectra of **1**, **4-4''** and **1''** (left) and their corresponding PXRD patterns (right).

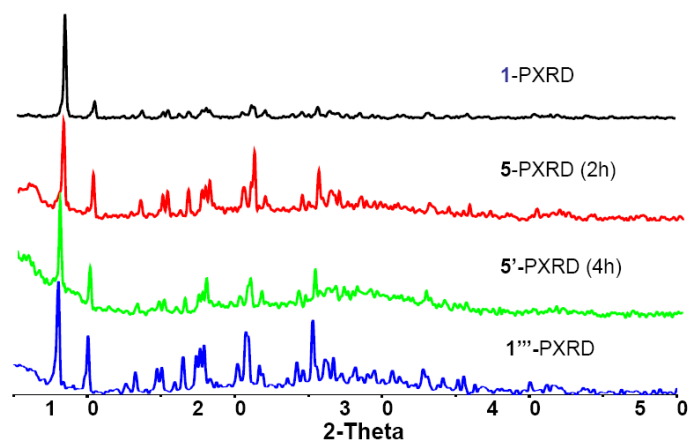
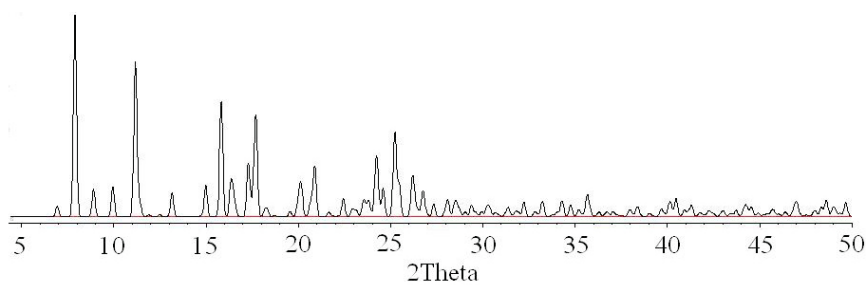
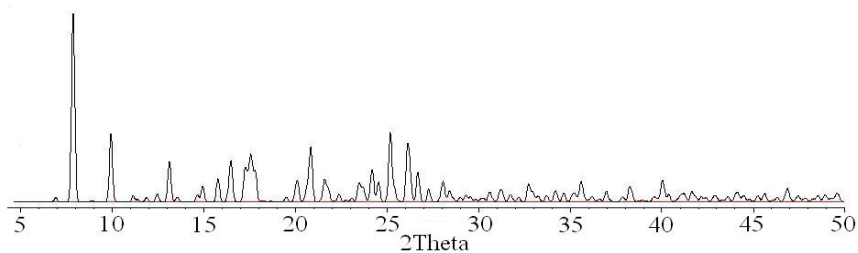


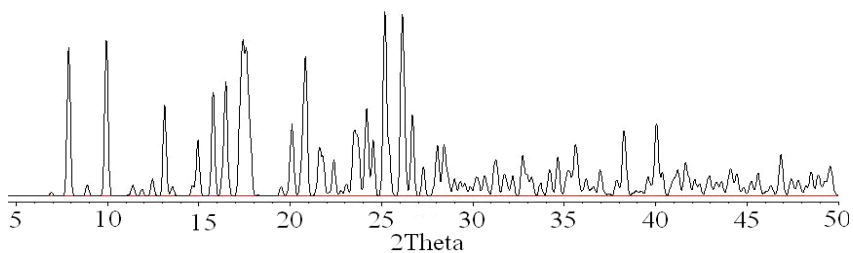
Figure S9. The PXRD patterns of the exchanged solids of **5** and **5'** are identical to that of **1**, suggesting the framework to be intact upon anion exchange.



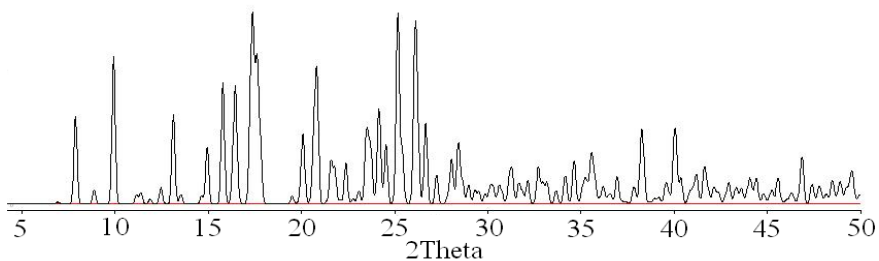
(a)



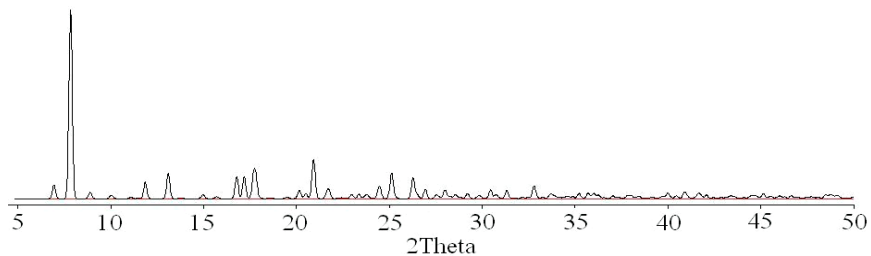
(b)



(c)



(d)



(e)

Figure S10. The calculated PXRD patterns of **2** (a), **3** (b), **3'** (c), **3''** (d) and **4** (e) are identical to those of experimental patterns, suggesting the framework to be stable during the iodine species enrichment.

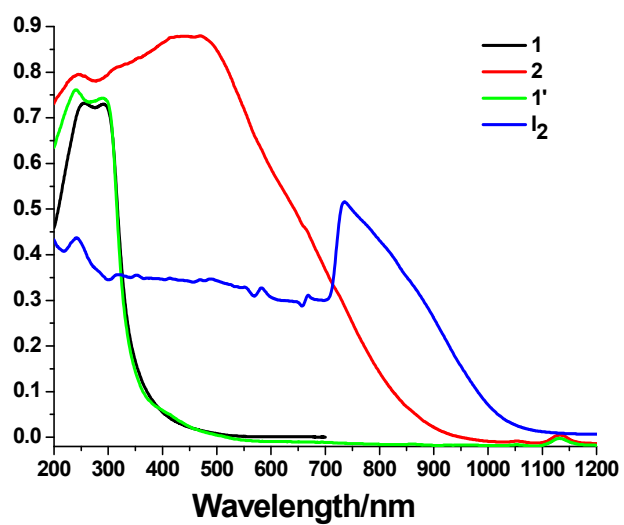


Figure S11. Solid state UV-vis spectra of **1**, **2**, **1'** and I₂ molecules.