## Supplementary Material (ESI) for CrystEngComm 2020.

Five water-stable luminescent $\mathrm{Cd}^{\mathrm{II}}$-based metal-organic frameworks as sensors for highly sensitive and selective detection of acetylacetone, $\mathrm{Fe}^{3+}$ and $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ ions

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Table S1a Crystal data and structure refinements for the 1-3

| Cd-MOFs | $\mathbf{1}$ | $\mathbf{2}$ | $\mathbf{3}$ |
| :--- | :--- | :--- | :--- |
| Chemical formula | $\mathrm{C}_{26} \mathrm{H}_{20} \mathrm{CdCl}_{2} \mathrm{~N}_{4} \mathrm{O}_{4}$ | $\mathrm{C}_{54} \mathrm{H}_{44} \mathrm{Cd}_{2} \mathrm{Cl}_{4} \mathrm{~N}_{8} \mathrm{O}_{8}$ | $\mathrm{C}_{45} \mathrm{H}_{34.5} \mathrm{Cd}_{2} \mathrm{Cl}_{4} \mathrm{~N}_{6} \mathrm{O}_{10.25}$ |
| Formula weight | 635.76 | 1299.57 | 1216.94 |
| Crystal system | monoclinic | Monoclinic | Monoclinic |
| Space group | $P 2_{1} / n$ | $P_{2} / n$ | $P 2_{1} / n$ |
| $a(\AA)$ | $9.304(2)$ | $14.993(3)$ | $18.478(4)$ |
| $b(\AA)$ | $15.944(3)$ | $21.331(4)$ | $9.489(2)$ |
| $c(\AA)$ | $17.445(4)$ | $16553(2)$ | $26.833(4)$ |
| $\alpha\left({ }^{\circ}\right)$ | 90 | 90 | 90 |
| $\beta\left({ }^{\circ}\right)$ | $94.552(2)$ | $98.640(2)$ | $91.811(2)$ |
| $\gamma\left({ }^{\circ}\right)$ | 90 | 90 | 90 |
| $V\left(\AA^{3}\right)$ | $2579.84(11)$ | $5224.19(16)$ | $4702.54(16)$ |
| $Z$ | 4 | 4 | 4 |
| $D_{\text {calcd }}\left(\mathrm{g} /\right.$ cm $\left.{ }^{3}\right)$ | 1.637 | 1.652 | 1.719 |
| Absorption coefficient, mm ${ }^{-1}$ | 1.094 | 1.082 | 1.196 |
| $F(000)$ | 1272 | 2608 | 2370 |
| Crystal size, mm | $0.27 \times 0.26 \times 0.23$ | $0.24 \times 0.22 \times 0.20$ | $0.26 \times 0.22 \times 0.21$ |
| $\theta$ range, deg | $4.684-61.052$ | $4.412-61.112$ | $4.41-61.152$ |
| Index range $h, k, l$ | $-13 / 11,-22 / 22,-24 / 23$ | $-21 / 21,-30 / 29,-15 / 23$ | $-25 / 25,-12 / 13,-36 / 35$ |
| Reflections collected | 37137 | 77199 | 70559 |
| Independent reflections $\left(\mathrm{R}_{\text {int }}\right)$ | $7603(0.0380)$ | $15324(0.0595)$ | $13816(0.0376)$ |
| Data/restraint/parameters | $7603 / 0 / 334$ | $15324 / 0 / 687$ | $13816 / 82 / 623$ |
| Goodness-of-fit on $F^{2}$ | 1.023 | 1.031 | 0.989 |
| Final $\mathrm{R}_{1}, w \mathrm{R}_{2}(I>2 \sigma(I))$ | $0.0300,0.0690$ | $0.0472,0.1192$ | $0.0363,0.0796$ |
| Largest diff. peak and hole | $0.68,-0.66$ | $2.11,-1.39$ | $1.17,-0.96$ |
|  |  |  |  |

Table S1b Crystal data and structure refinements for the $\mathbf{4}$ and 5

| Cd-MOFs | $\mathbf{4}$ | $\mathbf{5}$ |
| :--- | :--- | :--- |
| Chemical formula | $\mathrm{C}_{38} \mathrm{H}_{30} \mathrm{CdCl}_{2} \mathrm{~N}_{6} \mathrm{O}_{4}$ | $\mathrm{C}_{20} \mathrm{H}_{17} \mathrm{Cd}_{0.5} \mathrm{ClN}_{3} \mathrm{O}_{2}$ |
| Formula weight | 870.33 | 423.02 |
| Crystal system | Triclinic | monoclinic |
| Space group | $P \bar{l}$ | $C 2 / c$ |
| $a(\AA)$ | $9.628(6)$ | $13.1061(5)$ |
| $b(\AA)$ | $10.279(4)$ | $16.0142(5)$ |
| $c(\AA)$ | $18.731(9)$ | $17.5495(7)$ |
| $\alpha\left({ }^{\circ}\right)$ | $91.228(4)$ | 90 |
| $\beta\left({ }^{\circ}\right)$ | $101.525(4)$ | $97.736(4)$ |
| $\gamma\left({ }^{\circ}\right)$ | $90.458(4)$ | 90 |
| $V\left(\AA^{3}\right)$ | $1815.83(16)$ | $1051.6(2)$ |
| $Z$ | 2 | 8 |
| $D_{\text {calcd }}\left(\mathrm{g} / \mathrm{cm}{ }^{3}\right)$ | 1.564 | 1.540 |
| Absorption coefficient, mm ${ }^{-1}$ | 0.805 | 0.796 |
| $F(000)$ | 870 | 1720 |
| Crystal size, mm | $0.26 \times 0.23 \times 0.22$ | $0.20 \times 0.16 \times 0.12$ |
| $\theta$ range, deg | $5.326-62.064$ | $4.452-61.162$ |
| Index range $h, k, l$ | $-13 / 13,-14 / 14,-26 / 26$ | $-18 / 18,-22 / 22,-24 / 24$ |
| Reflections collected | 42306 | 26620 |
| Independent reflections $\left(\mathrm{R}_{\text {int }}\right)$ | $9988(0.0763)$ | $5301(0.0524)$ |
| Data/restraint/parameters | $9988 / 0 / 460$ | $5301 / 639 / 240$ |
| Goodness-of-fit on $F^{2}$ | 1.036 | 1.048 |
| Final $\mathrm{R}_{1}, w \mathrm{R}_{2}(I>2 \sigma(I))$ | $0.0735,0.1846$ | $0.0458,0.1295$ |
| Largest diff. peak and hole | $2.31,-0.89$ | $0.85,-1.13$ |
|  |  |  |

Table S2a Selected Bond Lengths [ $\AA$ ] and Angles [ ${ }^{\circ}$ ] for the $\mathbf{1}$ and $\mathbf{2}$

| Parameter | Value | Parameter | Value |
| :---: | :---: | :---: | :---: |
| 1 |  |  |  |
| Cd1-O1/O2 | 2.201(2) | Cd1-N1 | 2.236(2) |
| Cd1-O3B/O4B | 2.227(2) | Cd1-N4A | 2.249(2) |
| O1-Cd1-O4B | 121.17(7) | O1-Cd1-N1 | 121.27(6) |
| O1-Cd1-N4A | 99.10(6) | O4B-Cd1-N1 | 94.50(6) |
| O4B-Cd1-N4A | 111.32(7) | N1-Cd1-N4A | 109.72(7) |
| 2 |  |  |  |
| Cd1-O1/O1A | 2.249(2) | Cd1-O2/O2A | 2.615(2) |
| Cd1-N1/N1A | 2.099(2) | Cd2-O5/O5D | 2.174(2) |
| Cd2-N3/N3D | 2.221(3) | Cd3-07/O7F | 2.175(2) |
| Cd3-N5/N5F | 2.210(3) | Cd4-O4B/O4C | 2.407(2) |
| Cd4-O3B/O3C | 2.341(2) | Cd4-N8/N8G | 2.239(2) |
| O4B-Cd4-O4C | 128.09(11) | N8-Cd4-O4B | 99.64(9) |
| O3C-Cd4-O4C | 55.34(8) | N8-Cd4-O4C | 114.79(8) |
| O3B-Cd4-O4B | 55.34(8) | N8-Cd4-O3B | 168.92(9) |
| O3C-Cd4-O4B | 85.06(8) | N8G-Cd4-O3C | 91.23(9) |
| O3B-Cd4-O4C | 85.06(8) | N8-Cd4-O3B | 91.23(9) |
| O3B-Cd4-O3C | 83.16(12) | N8G-Cd4-O3B | 168.92(9) |
| N8G-Cd4-O4B | 114.79(8) | N8G-Cd4-N8 | 95.81(13) |
| N8G-Cd4-O4C | 99.64(9) | O1-Cd1-N1A | 116.89(8) |
| O1A-Cd1-O1 | 122.62(12) | $\mathrm{O} 1-\mathrm{Cd} 1-\mathrm{N} 1$ | 100.00(8) |
| O1-Cd1-O2 | 53.12(7) | $\mathrm{O} 2-\mathrm{Cd} 1-\mathrm{O} 2 \mathrm{~A}$ | 82.68(11) |
| O1A-Cd1-O2A | 53.12(7) | N1-Cd1-O2A | 94.99(8) |
| O1A-Cd1-O2 | 83.06(8) | N1A-Cd1-O2A | 153.13(8) |
| $\mathrm{O} 1-\mathrm{Cd} 1-\mathrm{O} 2 \mathrm{~A}$ | 83.06(8) | N1A-Cd1-O2 | 94.98(8) |
| O1A-Cd1-N1 | 116.89(8) | $\mathrm{N} 1-\mathrm{Cd} 1-\mathrm{O} 2$ | 153.13(8) |
| O1A-Cd1-N1A | 100.00(8) | N1-Cd1-N1A | 98.63(13) |
| O7F-Cd3-O7 | 102.13(12) | O5-Cd2-O5D | 107.25(12) |
| O7-Cd3-N5F | 118.60(9) | O5-Cd2-N3D | 119.32(10) |
| O7F-Cd3-N5F | 105.67(9) | O5D-Cd2-N3D | 102.00(9) |
| O7F-Cd3-N5 | 118.60(9) | O5-Cd2-N3 | 101.99(9) |
| O7-Cd3-N5 | 105.67(9) | O5D-Cd2-N3 | 119.32(10) |
| N5-Cd3-N5F | 106.88(14) | N3D-Cd2-N3 | 107.95(15) |

symmetry code: A: $-x, 1-y, 1-z, \mathrm{~B}: 0.5-x,-0.5+y, 0.5-z$ for $1 ; \mathrm{A}: 0.5-x, y, 0.5-z ; \mathrm{B}: 1-x,-y, 1-z ; \mathrm{C}: 0.5+x,-y$, $1.5+z, \mathrm{D}: 0.5-x, y, 1.5-z ; \mathrm{F}: 0.5-x, y, 2.5-z, \mathrm{G}: 1.5-x, y, 2.5-z$ for 2.

Table S2b Selected bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for Cd-MOFs 3-4.

| Parameter | Value | Parameter | Value |
| :---: | :---: | :---: | :---: |
| 3 |  |  |  |
| Cd1-O1 | 2.265(2) | Cd1-N6B | 2.392(2) |
| Cd1-O2 | 2.629(2) | Cd2-N2 | 2.275(2) |
| Cd1-O3 | 2.328(2) | Cd2-O5 | 2.275(4) |
| Cd1-O4 | 2.5263(2) | Cd2-O6 | 2.581(5) |
| Cd1-O4A | 2.4207(2) | Cd2-O7C | 2.361(4) |
| Cd1-N1 | 2.324(2) | Cd2-O8C | 2.420 (5) |
| Cd2-N4 | 2.233(2) | O4A-Cd1-O4 | 68.47(7) |
| $\mathrm{O} 1-\mathrm{Cd} 1-\mathrm{O} 2$ | 52.49(8) | N1-Cd1-O2 | 89.64(7) |
| $\mathrm{O} 1-\mathrm{Cd} 1-\mathrm{O} 3$ | 126.49(9) | N1-Cd1-O3 | 94.20(8) |
| O1-Cd1-O4 | 82.31(8) | N1-Cd1-O4A | 80.81(7) |
| O1-Cd1-O4A | 88.60(8) | N1-Cd1-O4 | 128.04(7) |
| O1-Cd1-N1 | 139.18(9) | N1-Cd1-N6B | 94.81(9) |
| O1-Cd1-N6B | 93.54(9) | N6B-Cd1-O2 | 80.96(8) |
| $\mathrm{O} 3-\mathrm{Cd} 1-\mathrm{O} 2$ | 163.73(8) | N4-Cd2-O7C | 98.68(12) |
| O3-Cd1-O4 | 53.38(7) | N4-Cd2-O8C | 130.47(18) |
| O3-Cd1-O4A | 99.20(8) | O5-Cd2-O6 | 51.45(12) |
| O3-Cd1-N6B | 82.96(9) | O5-Cd2-O7C | 83.87(17) |
| N2-Cd2-O5 | 106.83(16) | O5-Cd2-O8C | 91.41(19) |
| N2-Cd2-O6 | 101.8(2) | O7C-Cd2-O6 | 115.9(2) |
| N2-Cd2-O7C | 137.37(11) | O7C-Cd2-O8C | 53.56(11) |
| N2-Cd2-O8C | 84.49(10) | O8C-Cd2-O6 | 142.7(2) |
| N4-Cd2-N2 | 104.55(8) | N4-Cd2-O6 | 83.96(13) |
| N4-Cd2-O5 | 129.38(13) |  |  |
| 4 |  |  |  |
| Cd1-O2 | 2.398(4) | Cd1-N3C | $2.383(4)$ |
| Cd1-N1 | 2.327(4) | Cd1-N6D | $2.368(4)$ |
| Cd1-O1 | 2.413(4) | Cd1-O3 | $2.233(5)$ |
| $\mathrm{O} 2-\mathrm{Cd} 1-\mathrm{O} 1$ | 54.44(14) | N6D-Cd1-O1 | 87.55(16) |
| $\mathrm{N} 1-\mathrm{Cd} 1-\mathrm{O} 2$ | 146.49(14) | N6D-Cd1-N3C | 169.98(15) |
| N1-Cd1-O1 | 93.46(14) | O3-Cd1-O2 | 114.9(2) |
| N1-Cd1-N3C | 87.02(15) | O3-Cd1-N1 | 97.8(2) |
| N1-Cd1-N6D | 90.66(16) | O3-Cd1-O1 | 168.5(2) |
| $\mathrm{N} 3 \mathrm{C}-\mathrm{Cd} 1-\mathrm{O} 2$ | 80.24(15) | $\mathrm{O} 3-\mathrm{Cd} 1-\mathrm{N} 3 \mathrm{C}$ | 100.0(2) |
| $\mathrm{N} 3 \mathrm{C}-\mathrm{Cd} 1-\mathrm{O} 1$ | 82.87(15) | O3-Cd1-N6D | 90.0(2) |
| N6D-Cd1-O2 | 96.56(16) |  |  |

symmetry code: A: $-x, 2-y, 1-z, \mathrm{~B}: 1-x, 2-y, 1-z, \mathrm{C}: 0.5+x, 0.5-y, 0.5+z$ for $\mathbf{3} ; \mathrm{C}: 1+x, y, z ; \mathrm{D}: x, 1+y, z$. for $\mathbf{4}$.

Table S2c Selected bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for Cd-MOFs 5.

| Parameter | Value | Parameter | Value |
| :--- | :--- | :--- | :--- |
| $\mathbf{5}$ |  |  |  |
| Cd1-N1/N1A | $2.283(2)$ | Cd1-O1/O1A | $2.382(2)$ |
| Cd1-O2/O2A | $2.382(2)$ | N11-Cd1-O2A | $133.14(12)$ |
| N1A-Cd1-N1 | $89.91(13)$ | N1-Cd1-O2A | $93.91(10)$ |
| N1-Cd1-O1A | $135.46(12)$ | O1A-Cd1-O1 | $114.2(2)$ |
| N1A-Cd1-O1 | $135.46(12)$ | O2A-Cd1-O1A | $53.56(11)$ |
| N11-Cd1-O1A | $93.20(10)$ | O2-Cd1-O1 | $53.56(10)$ |
| N1-Cd1-O1 | $93.20(10)$ | O2-Cd1-O1A | $90.98(15)$ |
| N1-Cd1-O2 | $133.14(12)$ | O2A-Cd1-O1 | $90.98(15)$ |
| N1A-Cd1-O2 | $93.91(10)$ | O2-Cd1-O2A | $115.8(2)$ |

symmetry code: A:1-x, $y, 1.5-z$ for 5.

Table S3 Hydrogen bonds ( $\AA$ ) and angles ( ${ }^{\circ}$ ) for the $\mathbf{1 / 2}$

| Donor-H $\cdots$ acceptor | $\mathrm{D}-\mathrm{H}$ | $\mathrm{H} \cdots \mathrm{A}$ | $\mathrm{D} \cdots \mathrm{A}$ | Angle |
| :--- | :--- | :--- | :--- | :--- |
| $\mathbf{1}$ |  |  |  |  |
| N2C-H2C $\cdots$ O3C | 0.86 | 1.94 | $2.743(3)$ | 156 |
| N3C-H3C $\cdots$ O2C | 0.86 | 1.98 | $2.770(3)$ | 153 |
| $\mathbf{2}$ |  |  |  |  |
| N2H-H3H $\cdots$ O3H | 0.86 | 1.89 | $2.735(3)$ | 167 |
| N4I-H3I $\cdots$ O2I | 0.86 | 1.96 | $2.758(4)$ | 154 |
| N6J-H6J $\cdots$ O6J | 0.86 | 1.95 | $2.745(4)$ | 153 |
| N7J-H7J $\cdots$ O8J | 0.86 | 2.04 | $2.853(3)$ | 156 |

Symmetry codes for 1: $\mathrm{C}=1-x, 1-y, 1-z ;$ Symmetry codes for 2: $\mathrm{H}=-x-,-y,-z ; \mathrm{I}=0.5+x,-y, 0.5+z$; $\mathrm{J}=1-x, 1-y, 2-z$.

Table S4. Comparison of the sensitivities of $\mathbf{1}$ and $\mathbf{2}$ for acac with related MOFs

| MOFs | LOD/M | Ref |
| :--- | :--- | :---: |
| $\left\{\left[\left(\mathrm{CH}_{3}\right)_{2} \mathrm{NH}_{2}\right]\left[\mathrm{Zn}(\mathrm{FDA})(\mathrm{BTZ})_{2}\right]\right\}_{\mathrm{n}}$ | $6.47 \times 10^{-7}$ | $[9]$ |
| $\left\{\left[\mathrm{Zn}_{3}(\mathrm{bbib})_{2}(\mathrm{ndc})_{3}\right] \cdot 2 \mathrm{DMF} \cdot 2 \mathrm{H}_{2} \mathrm{O}\right\}_{\mathrm{n}}$ | $0.10 \times 10^{-7}$ | $[5]$ |
| $\left\{\left[\mathrm{Co}_{1.5}(\mathrm{TBIP})_{1.5}(\mathrm{~L})\right] \cdot 0.5 \mathrm{H}_{2} \mathrm{O}\right\}_{\mathrm{n}}$ | $0.023 \times 10^{-6}$ | $[6]$ |
| $\mathbf{2}$ | $6.36 \times 10^{-7}$ | This work |
| $\mathbf{3}$ | $8.76 \times 10^{-7}$ | This work |

$\mathrm{H}_{2} \mathrm{FDA}=$ furan-2,5-dicarboxylic acid, $\mathrm{HBTZ}=1 \mathrm{H}$-benzotriazole, bbib $=1,3$-bis(benzimidazolyl)benzene, $\mathrm{H}_{2}$ ndc
$=1,4$-naphthalenedicarboxylic acid, $\mathrm{L}=1,3$-bis(5,6-dimethylbenzimidazol-1-yl)propane, and $\mathrm{H}_{2} \mathrm{TBIP}=5$-tert-
butylisophthalic acid.

Table S5. Comparison of the sensitivities of $\mathbf{2}$ with previously reported MOFs to $\mathrm{Fe}^{3+}$


4,4,(hexafluoroisopropylidene)bis(benzoic acid), $\mathrm{Htrz}=1 \mathrm{H}-1,2,3$-triazole; $\mathrm{H}_{2} \mathrm{~L}=8$-hydroxyquinolinate derivative.

Table S6. Comparison of the sensitivities of $\mathbf{3}$ with previously reported MOFs to

| $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ ions |  |  |
| :--- | :--- | :---: |
| MOFs | LOD/M | Ref |
| $\left\{\left[\mathrm{Co}_{1.5}(\mathrm{TBIP})_{1.5}(\mathrm{~L})\right] \cdot 0.5 \mathrm{H}_{2} \mathrm{O}\right\}_{\mathrm{n}}$ | $2.09 \times 10^{-4}$ | $[6]$ |
| $\left\{\left[\mathrm{Cd}_{2}(\mathrm{~L})(\mathrm{DMA})\right] \cdot\left[\mathrm{H}_{2} \mathrm{~N}(\mathrm{Me})_{2}\right]\right\}_{\mathrm{n}}$ | $2.54 \times 10^{-3}$ | $[4]$ |
| $\mathrm{Zr}_{6} \mathrm{O}_{4}(\mathrm{OH})_{7}\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}(\mathrm{BTBA})_{3}$ | $1.5 \times 10^{-6}$ | $[8]$ |
| $\mathbf{2}$ | $1.99 \times 10^{-5} \mathrm{M}$ | This work |

$\mathrm{L}=$ 1,3-bis(5,6-dimethylbenzimidazol-1-yl)propane, and $\mathrm{H}_{2}$ TBIP $=$ 5-tert-butylisophthalic acid; $\mathrm{H}_{5} \mathrm{~L}=$ 2,4-
di(3,5dicarboxylphenyl)benzoic acid; $\mathrm{H}_{3} \mathrm{BTBA}=4,4^{\prime}, 4^{\prime \prime}$-( $1 \mathrm{Hbenzo}[\mathrm{d}]$ imidazole-2,4,7-triyl)tribenzoic acid.

Fig. S1. (a) The $\mathrm{DCTP}^{2-}$ anions create a 1 D infinite $[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ chain by linking adjacent $\mathrm{Cd}^{\mathrm{II}}$ ions in $\mathbf{1}$; the binuclear $\left[\mathrm{Cd}_{2}(\mathrm{~L})_{2}\right]$ unit was formed by L 1 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms; (c) the 3D supramolecular network of $\mathbf{1}$ formed by two hydrogen bonds interactions (Pink dotted line).

Fig. S2. (a) two varying 1D chains, named as $[(\mathrm{Cd} 1)(\mathrm{Cd} 2)(\mathrm{L} 2)]_{\mathrm{n}},\left[(\mathrm{Cd} 3)(\mathrm{Cd} 4)(\mathrm{L} 2)_{2}\right]_{\mathrm{n}}$ were formed by L2 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in 2; (b) Two 1D "V" like chains( $[(\mathrm{Cd} 1)(\mathrm{Cd} 4)(\mathrm{DCTP})]_{\mathrm{n}}$ and $\left[(\mathrm{Cd} 2)(\mathrm{Cd} 3)(\mathrm{DCTP}]_{\mathrm{n}}\right)$ with the surrounding $\mathrm{Cd}^{\mathrm{II}}$ centers in 2 (c) the 3D supramolecular network of 2 formed by two hydrogen bonds interactions (pink dotted line).

Fig. S3. (a) The $\mathrm{DCTP}^{2-}$ anions connect the adjacent $\mathrm{Cd}^{\mathrm{II}}$ ions using these two coordination modes in 3; (b) The $\mu_{3}$-bridging L3 ligands adopt the cis-conformation to form a rhombus unit $\left[\mathrm{Cd}_{4}(\mathrm{~L} 3)_{2}\right]$ in $\mathbf{3}$. (c) 3,3,4,5-connected topology of $\mathbf{3}$ (the green, blue and red nodes represent $\mathrm{Cd}^{\mathrm{II}}$ center, L3 ligands and DCTP ${ }^{2-}$ anions, respectively). Fig. S4. (a) Two different DCTP ${ }^{2-}$ anions link adjacent $\mathrm{Cd}^{\mathrm{II}}$ atoms to form a 1 D infinite chain $[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ in 4; (b) 2D network $[\mathrm{Cd}(\mathrm{L} 4)]_{\mathrm{n}}$ is formed by using $\mu_{3^{-}}$ bridging L4 ligands with a cis-conformation fashion to connect $\mathrm{Cd}^{\mathrm{II}}$ ions; (c) an rarely 2-nodal (3,5)-connected gra topological network of 4 (the green and blue represent $\mathrm{Cd}^{\mathrm{II}}$ center and L3 ligands, respectively).

Fig. S5. (a) 1D"V" like chains, named as 1D $[\mathrm{Cd}(\mathrm{L} 5)]_{\mathrm{n}}$ is formed by L 5 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in 5; (b) 1D "V" like chains $[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ is formed by DCTP ${ }^{2-}$ ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in 5.

Fig. S6. The infrared spectrum of Cd-MOFs 1-5.
Fig. S7. The PXRD pattern of the bulk sample is consistent with the simulated pattern of the single crystal structure in Cd-MOFs 1-5.

Fig. S8. Soild luminescence lifetime of Cd-MOFs 1-5.
Fig. S9. Time-dependent emission spectra of 2 (a) and 3 (b) suspended in aqueous solutions.

Fig. S10. PXRD patterns of $\mathbf{2}$ and $\mathbf{3}$ under simulated conditions.
Fig. S11. The change of the fluorescence emission intensity of 2 (a) and 3 (b) in different pH solutions.

Fig. S12. The PXRD patterns of $\mathbf{2}$ (a) and $\mathbf{3}$ (b) were measured in different solvents.
Fig. S13. Spectral overlap between the absorption spectra of acac ions and the excitation spectra of $\mathbf{2}$ and $\mathbf{3}$.

Fig. S14. In 2, the time required for the quenching efficiency of $\mathrm{Fe}^{3+}$ ions to reach the maximum.

Fig. S15. The PXRD patterns of 2 sample was immersed in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ solution containing $\mathrm{Fe}^{3+}$ ions and other common cations.

Fig. S16. Spectral overlap between the absorption spectra of $\mathrm{Fe}^{3+}$ ions and the excitation spectra of $\mathbf{2}$.

Fig. S17. In 3, the time required for the quenching efficiency of $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ anions to reach the maximum.

Fig. S18. The PXRD patterns of $\mathbf{3}$ sample was immersed in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ solution containing $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ anions and other common anions.

Fig. S19. Spectral overlap between the absorption spectra of $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ anions and the excitation spectra of $\mathbf{3}$.

Fig. S20. TGA curves of Cd-MOFs $\mathbf{1 - 5 .}$
Fig. S21. Comparison of the quenching efficiency of $\mathbf{2}$ for sensing acac $/ \mathrm{Fe}^{3+}$, and $\mathbf{3}$ for acac/ $/ \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ over three cycles.

Fig. S22. (a) Effects of pH on the fluorescence maxima of $\mathbf{2}+\mathrm{acac}$ (circle) and $\mathbf{2}+$ $\mathrm{Fe}^{3+}$ (triangle); (a) Effects of pH on the fluorescence maxima of $\mathbf{3}+$ acac (circle) and $3+\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ (triangle). Solvent: $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}(1: 1, \mathrm{v} / \mathrm{v})$.

Fig. S23. The EDX patterns of $\mathbf{2}$ and $\mathbf{3} ; \mathbf{2}+$ acac, $\mathbf{3}+$ acac; $\mathbf{2}+\mathrm{Fe}^{3+}, \mathbf{3}+\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$, respectively.

(a)

(b)

(c)

Fig. S1. (a) The DCTP ${ }^{2-}$ anions create a 1D infinite $[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ chain by linking adjacent $\mathrm{Cd}^{\mathrm{II}}$ ions in $\mathbf{1}$; the binuclear $\left[\mathrm{Cd}_{2}(\mathrm{~L} 1)_{2}\right]$ unit was formed by L 1 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms; (c) the 3D supramolecular network of $\mathbf{1}$ formed by two hydrogen bonds interactions (Pink dotted line).

(a)

(b)

(c)

Fig. S2. (a) two varying 1D chains, named as $[(\mathrm{Cd} 1)(\mathrm{Cd} 2)(\mathrm{L} 2)]_{\mathrm{n}},\left[(\mathrm{Cd} 3)(\mathrm{Cd} 4)(\mathrm{L} 2)_{2}\right]_{\mathrm{n}}$ were formed
by L2 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in $\mathbf{2}$; (b) Two 1D "V" like chains( $[(\mathrm{Cd} 1)(\mathrm{Cd} 4)(\mathrm{DCTP})]_{\mathrm{n}}$ and
$\left[(\mathrm{Cd} 2)(\mathrm{Cd} 3)(\mathrm{DCTP}]_{\mathrm{n}}\right)$ with the surrounding $\mathrm{Cd}^{\mathrm{II}}$ centers in $2(\mathrm{c})$ the 3 D supramolecular network of
$\mathbf{2}$ formed by two hydrogen bonds interactions (pink dotted line).


Mode I


Mode II
(a)

(b)


(c)

Fig. S3. (a) The DCTP ${ }^{2-}$ anions connect the adjacent $\mathrm{Cd}^{\mathrm{II}}$ ions using these two coordination modes in $\mathbf{3}$; (b) The $\mu_{3}$-bridging L3 ligands adopt the cis-conformation to form a rhombus unit
$\left[\mathrm{Cd}_{4}(\mathrm{~L} 3)_{2}\right]$ in 3. (c) 3,3,4,5-connected topology of $\mathbf{3}$ (the green, blue and red nodes represent $\mathrm{Cd}^{\mathrm{II}}$ center, L3 ligands and DCTP ${ }^{2-}$ anions, respectively).

(a)

(b)

(c)

Fig. S4. (a) Two different DCTP ${ }^{2-}$ anions link adjacent $\mathrm{Cd}^{\mathrm{II}}$ atoms to form a 1D infinite chain
$[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ in 4; (b) 2D network $[\mathrm{Cd}(\mathrm{L} 4)]_{\mathrm{n}}$ is formed by using $\mu_{3}$-bridging L 4 ligands with a cisconformation fashion to connect $\mathrm{Cd}^{\mathrm{II}}$ ions; (c) an rarely 2-nodal $(3,5)$-connected gra topological network of 4 (the green and blue represent $\mathrm{Cd}^{\mathrm{II}}$ center and L3 ligands, respectively).

(a)

(b)

Fig. S5. (a) 1D "V" like chains, named as 1D $[\mathrm{Cd}(\mathrm{L} 5)]_{\mathrm{n}}$ is formed by L 5 ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in $\mathbf{5}$; (b) 1 D "V" like chains $[\mathrm{Cd}(\mathrm{DCTP})]_{\mathrm{n}}$ is formed by DCTP2- ligands and $\mathrm{Cd}^{\mathrm{II}}$ atoms in $\mathbf{5}$.


Fig. S6. The infrared spectrum of Cd-MOFs 1-5.


Fig. S7. The PXRD pattern of the bulk sample is consistent with the simulated pattern of the single crystal structure in Cd-MOFs 1-5.


Fig. S8. Soild luminescence lifetime of Cd-MOFs 1-5.


Fig. S9. Time-dependent emission spectra of 2 (a) and $\mathbf{3}$ (b) suspended in aqueous solutions.

(a)


Fig. S10. PXRD patterns of $\mathbf{2}$ and $\mathbf{3}$ under simulated conditions.


Fig. S11. The change of the fluorescence emission intensity of $\mathbf{2}$ (a) and $\mathbf{3}$ (b) in different pH solutions.


Fig. S12. The PXRD patterns of 2 (a) and $\mathbf{3}$ (b) were measured in different solvents.


Fig. S13. Spectral overlap between the absorption spectra of acac ions and the excitation spectra of $\mathbf{2}$ and $\mathbf{3}$.


Fig. S14. In 2, the time required for the quenching efficiency of $\mathrm{Fe}^{3+}$ ions to reach the maximum.


Fig. S15. PXRD patterns of 2 (samples were immersed in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ solution containing $\mathrm{Fe}^{3+}$ ions and other common cations).


Fig. S16. Spectral overlap between the absorption spectra of $\mathrm{Fe}^{3+}$ ions and the excitation spectra of $\mathbf{2}$.


Fig. S17. In 3, the time required for the quenching efficiency of $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ anions to reach the maximum.


Fig. S18. The PXRD patterns of $\mathbf{3}$ sample was immersed in $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}$ solution containing $\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ anions and other common anions.


Fig. S19. Spectral overlap between the absorption spectra of $\mathrm{Cr}_{2} \mathrm{O}_{7}^{2-}$ anions and the excitation spectra of $\mathbf{3}$.


Fig. S20. TGA curves of Cd-MOFs $\mathbf{1 - 5}$.


Fig. S21. Comparison of the quenching efficiency of $\mathbf{2}$ for sensing acac $/ \mathrm{Fe}^{3+}$, and $\mathbf{3}$ for acac $/ \mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ over three cycles.


Fig. S22. (a) Effects of pH on the fluorescence maxima of $\mathbf{2}+$ acac (circle) and $\mathbf{2}+$ $\mathrm{Fe}^{3+}$ (triangle); (a) Effects of pH on the fluorescence maxima of $\mathbf{3}+$ acac (circle) and
$3+\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$ (triangle). Solvent: $\mathrm{EtOH} / \mathrm{H}_{2} \mathrm{O}(1: 1, \mathrm{v} / \mathrm{v})$.


Fig. S23. The EDX patterns of $\mathbf{2}$ and $\mathbf{3} ; \mathbf{2}+$ acac, $\mathbf{3}+\mathrm{acac} ; \mathbf{2}+\mathrm{Fe}^{3+}, \mathbf{3}+\mathrm{Cr}_{2} \mathrm{O}_{7}{ }^{2-}$,
respectively.

