

# Supporting Information

## **Influence of Interpenetration in Diamondoid MOFs on the Photoreactivity and Sensing Properties**

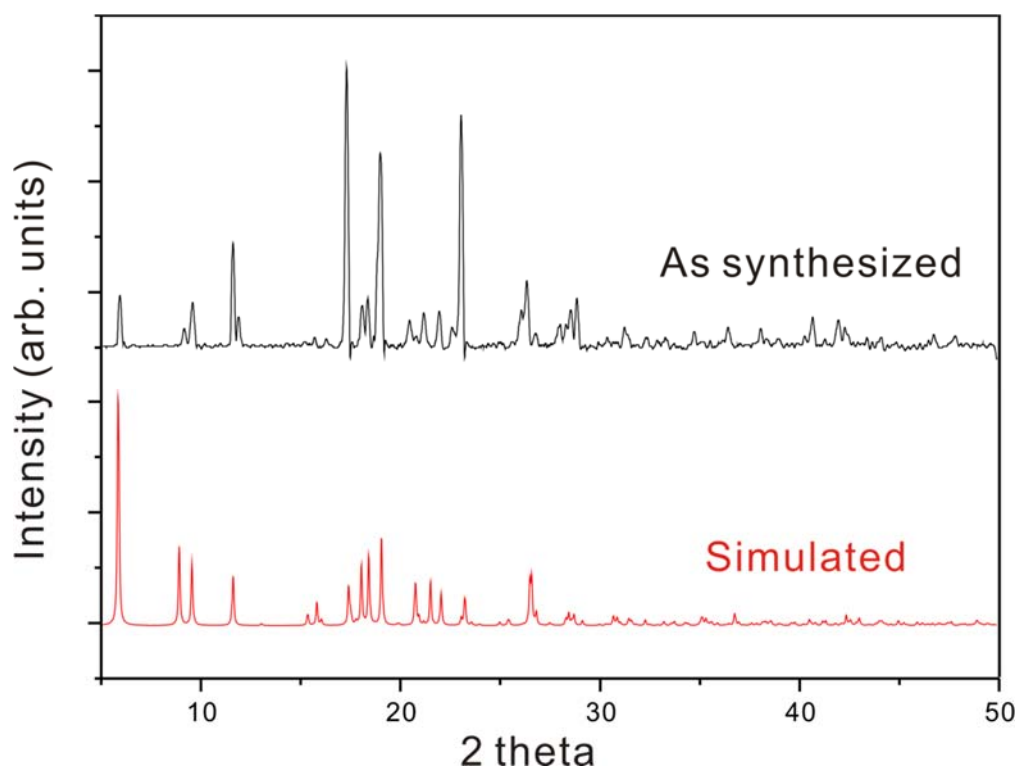
In-Hyeok Park,<sup>†</sup> Caroline Evania Mulijanto,<sup>‡</sup> Hyeong-Hwan Lee,<sup>†</sup> Yunji Kang,<sup>†</sup> Eunji Lee,<sup>†</sup> Anjana Chanthapally,<sup>‡</sup> Shim Sung Lee,<sup>\*,†</sup> and Jagadese J. Vittal<sup>\*,‡</sup>

<sup>†</sup>Department of Chemistry and Research Institute of Natural Science, Gyeongsang National University, Jinju 52828, S. Korea

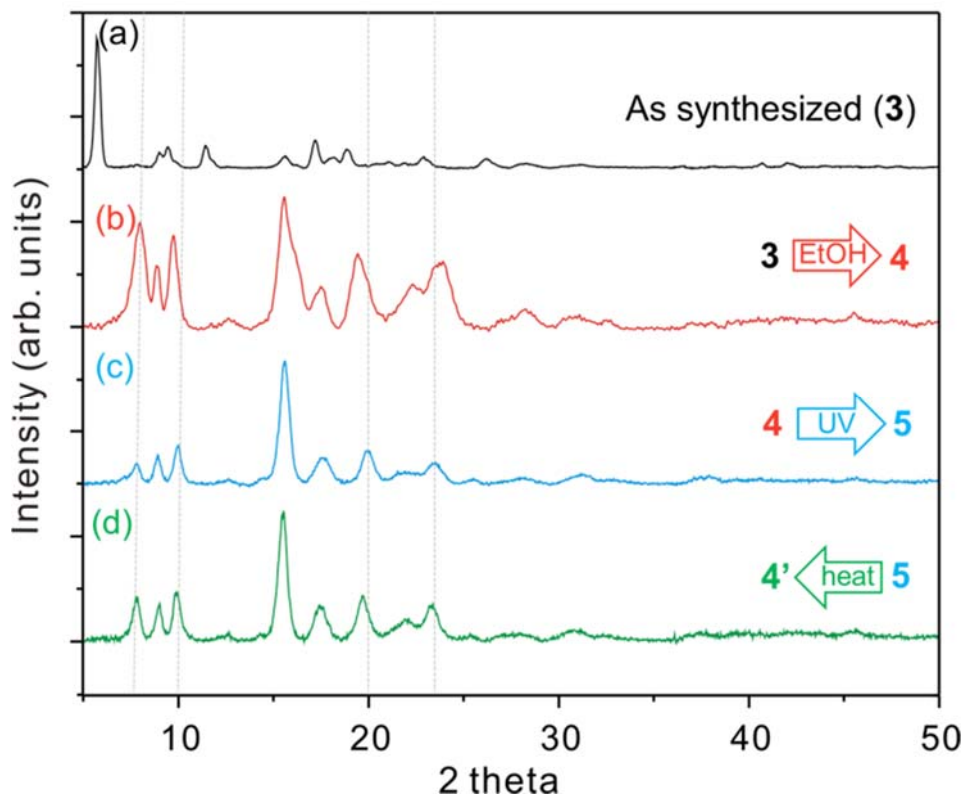
<sup>‡</sup>Department of Chemistry, National University of Singapore, 3 Science Drive 3, 11753, Singapore

**Table S1. Crytal Data for 3 (CCDC 1456992)**

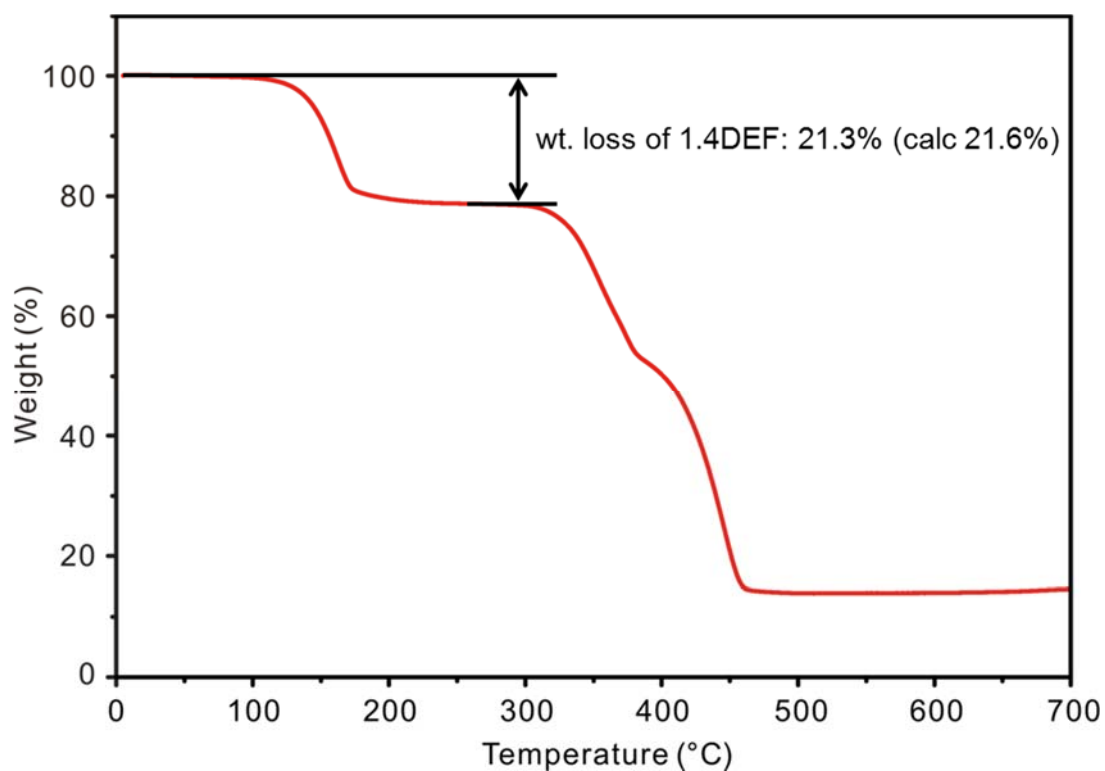
|  | <b>3</b>   |
|--|--|
| formula  | C <sub>38</sub> H <sub>42</sub> N <sub>4</sub> O <sub>6</sub> Zn |
| formula weight   | 716.12   |
| crystal system   | monoclinic   |
| space group  | <i>C2/c</i>  |
| <i>a</i> (Å)   | 31.3256(6)   |
| <i>b</i> (Å)   | 5.88880(10)  |
| <i>c</i> (Å)   | 20.4485(4)   |
| $\alpha$ (°)   | 90   |
| $\beta$ (°)  | 102.229(2)   |
| $\gamma$ (°)   | 90   |
| <i>V</i> (Å <sup>3</sup> )   | 3686.54(12)  |
| <i>Z</i>   | 4  |
| <i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )  | 1.290  |
| $\mu$ (mm <sup>-1</sup> )  | 0.716  |
| 2 $\theta$ <sub>max</sub> (°)  | 52.00  |
| reflections collected  | 27366  |
| independent reflections  | 9989 ( <i>R</i> <sub>int</sub> = 0.0311)                         |
| goodness-of-fit on <i>F</i> <sup>2</sup>   | 1.072  |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] | 0.0318, 0.0792   |
| <i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)                            | 0.0355, 0.0813   |



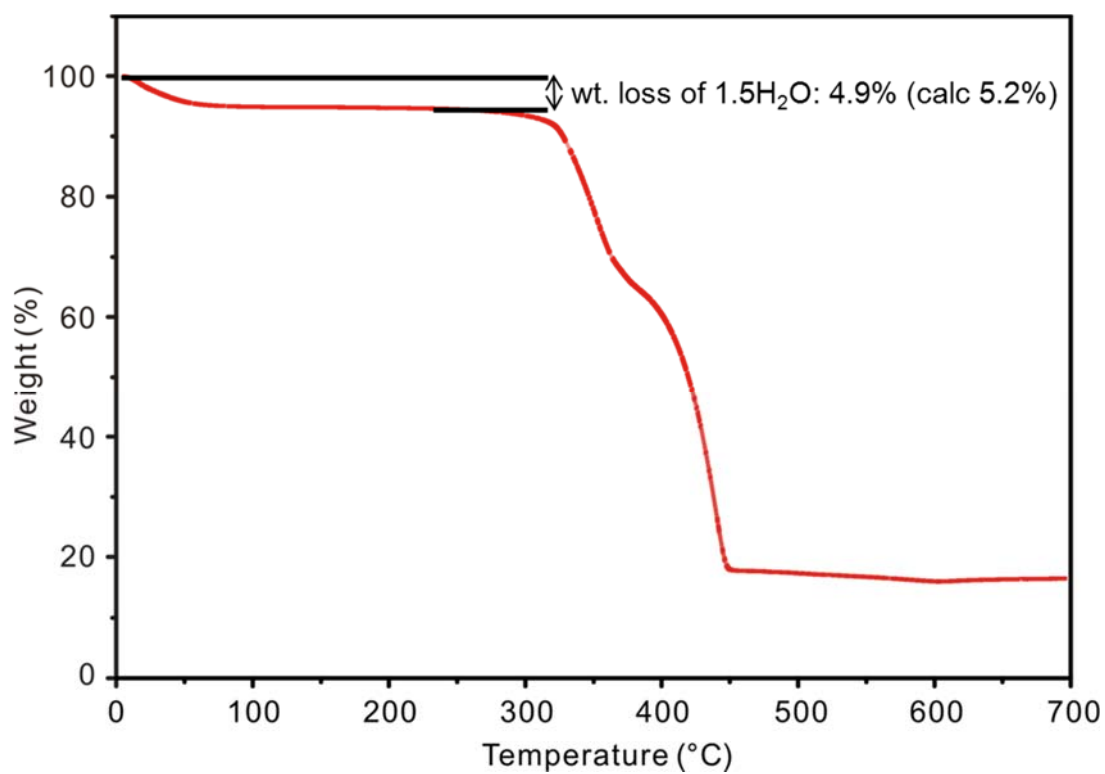
**Figure S1.** Comparison of PXRD patterns for **3**: (top) as synthesized and (bottom) simulated from the single crystal X-ray data. The deviations in these PXRD patterns may be due to the change of phase due to solvent loss during grinding during sample preparation.



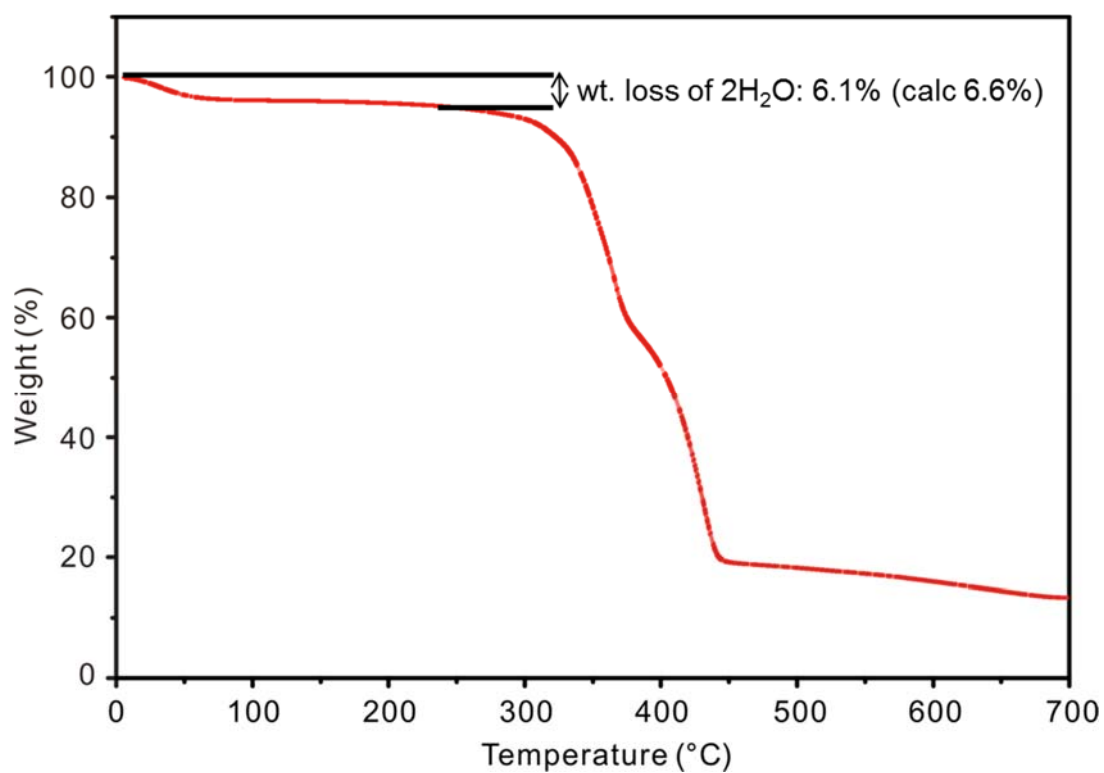
**Figure S2.** PXRD patterns for (a) **3**, (b) **4** (crystals of **3** after immersion in EtOH for 2 days), (c) **5** (crystals of **4** after UV irradiation for 2 days) and (d) **4'** (crystals of **5** after heat for 12 h).



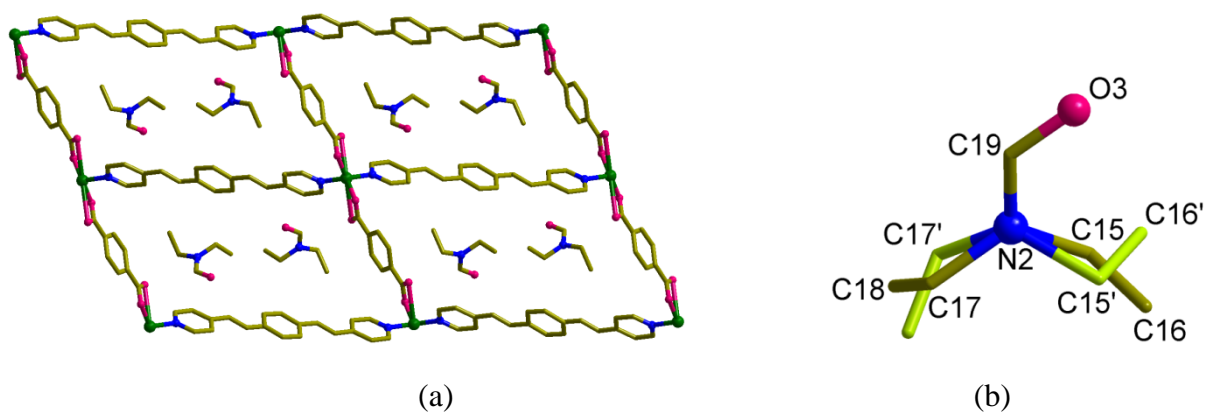
**Figure S3.** TGA curve of **3** with heating rate of 5 °C·min<sup>-1</sup> under N<sub>2</sub> flow.



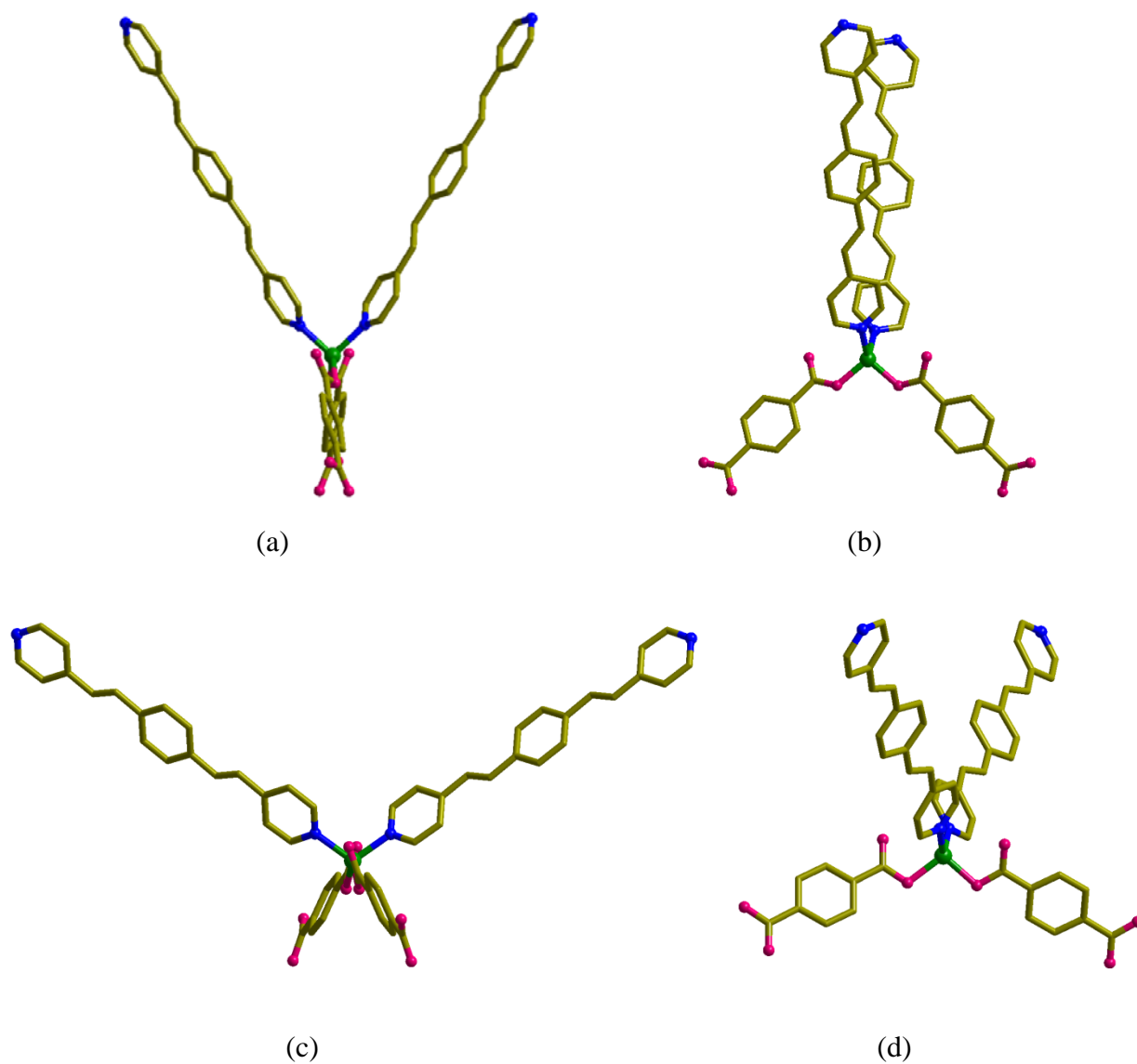
**Figure S4.** TGA curve of **4** with heating rate of 5 °C·min<sup>-1</sup> under N<sub>2</sub> flow.



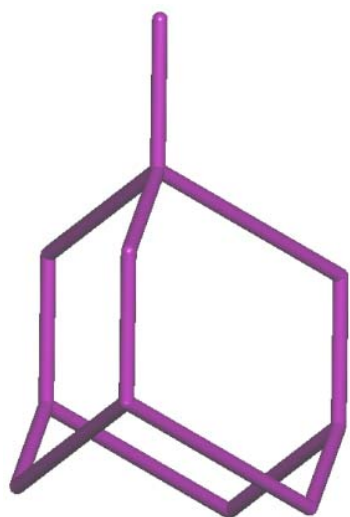
**Figure S5.** TGA curve of **5** with heating rate of 5 °C·min<sup>-1</sup> under N<sub>2</sub> flow.



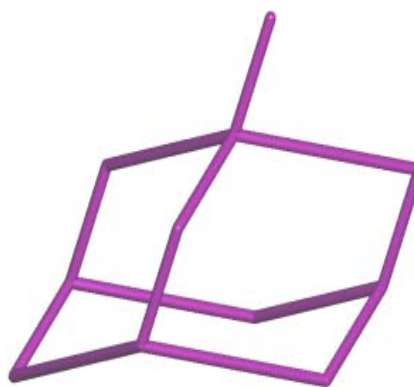
**Figure S6.** Structure of **3**: (a) A portion of the structure showing the arrangement of the guest DEF molecules. (b) Disordered DEF molecule.



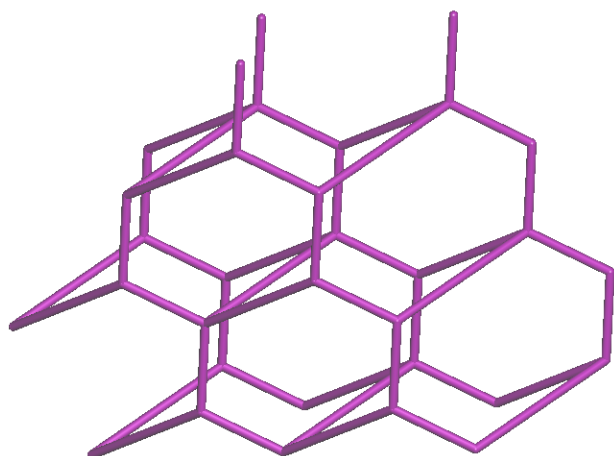
**Figure S7.** The structural comparison of coordination environments in (a) & (b) **1** and (c) & (d) **3**. The slip-stacked alignment arises from the relative orientations of the adjacent bpeb ligands which is governed by N-Zn-N angles.



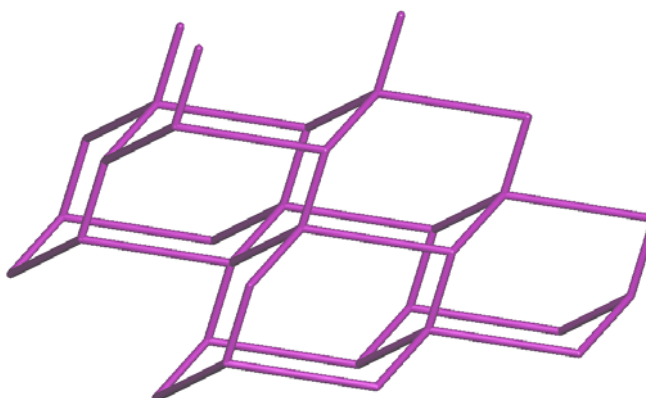
(a)



(b)

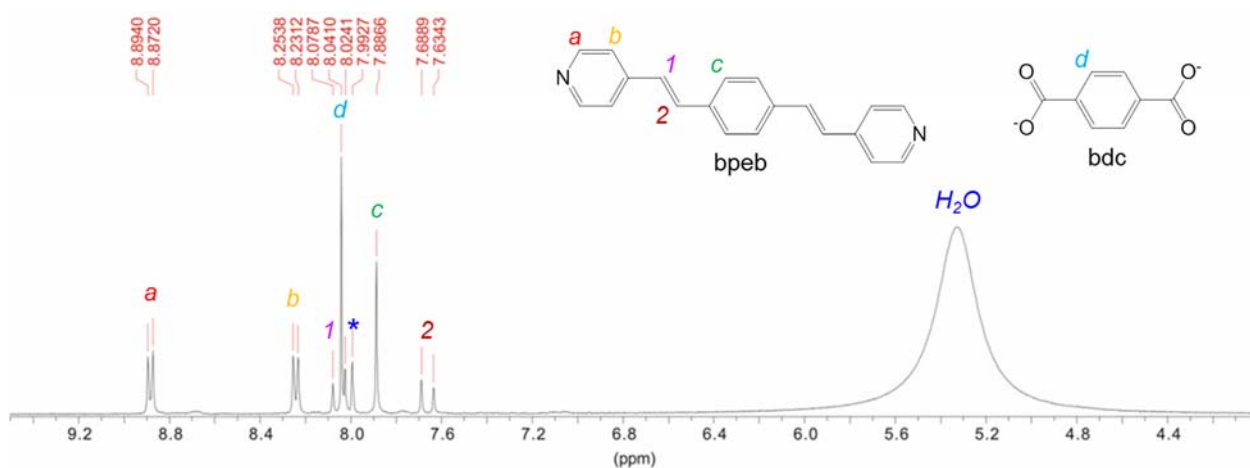


(c)

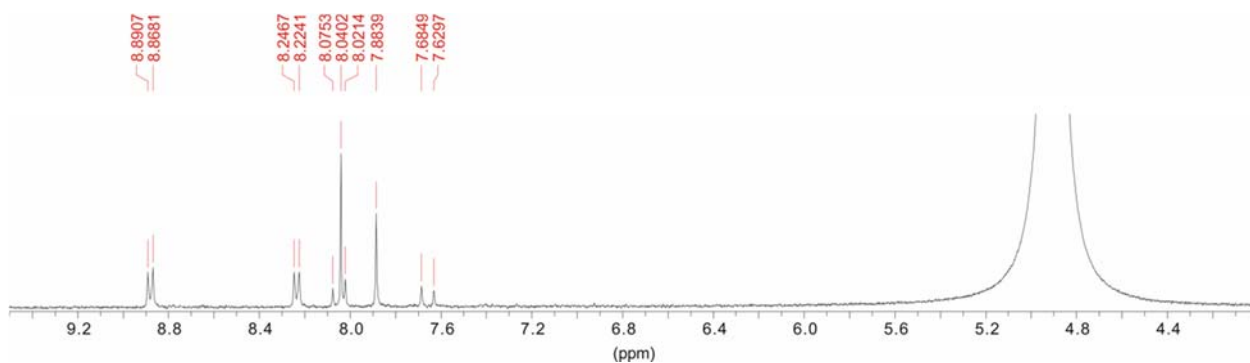


(d)

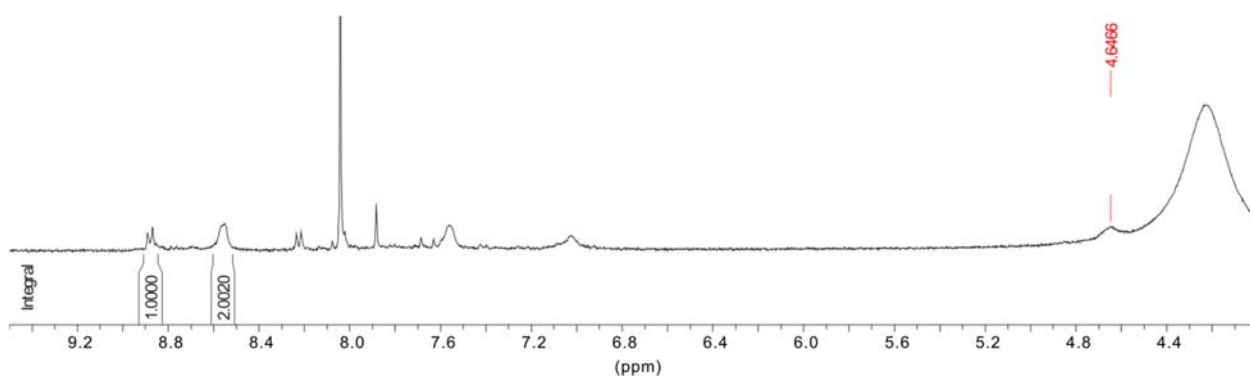
**Figure S8.** The single **dia** network in (a) **1** and (b) **3**. The **dia** topology in (c) **1** and (d) **3**.



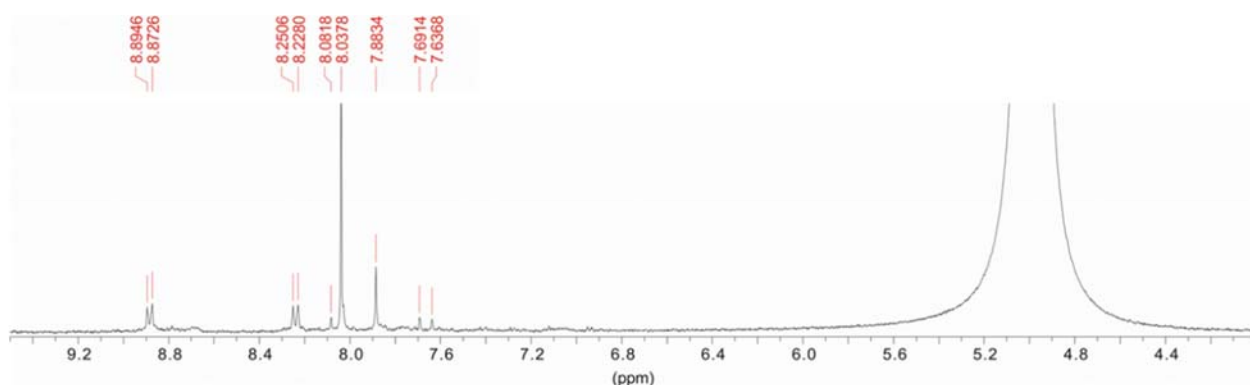
(a)



(b)



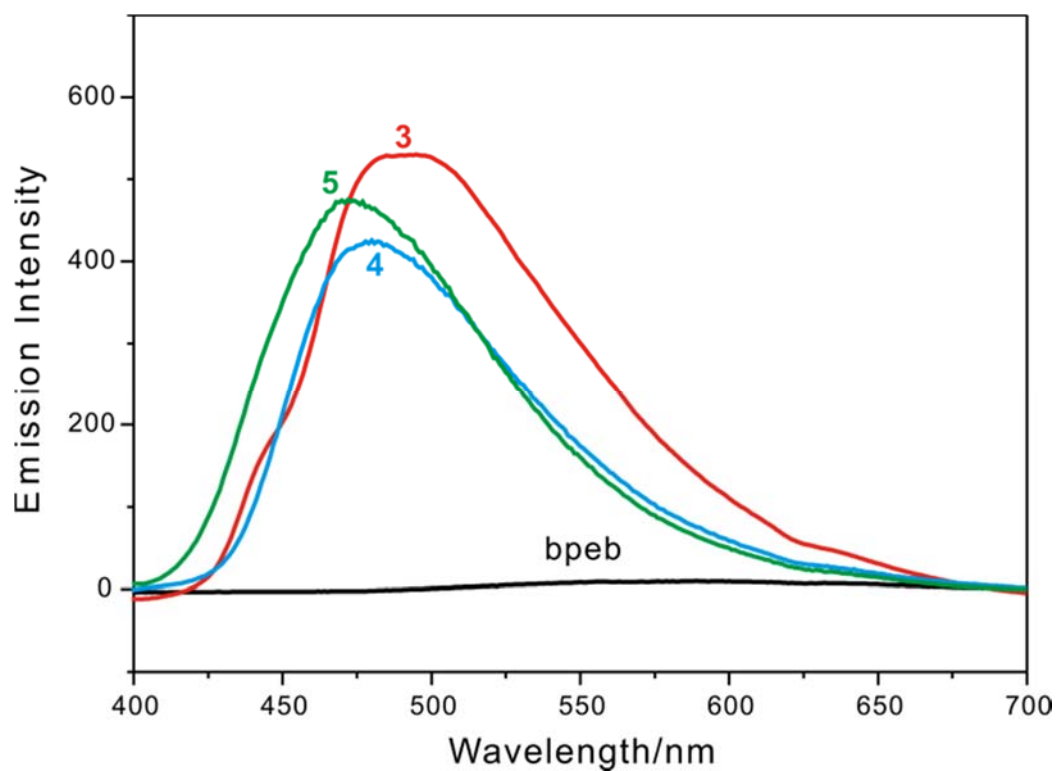
(c)



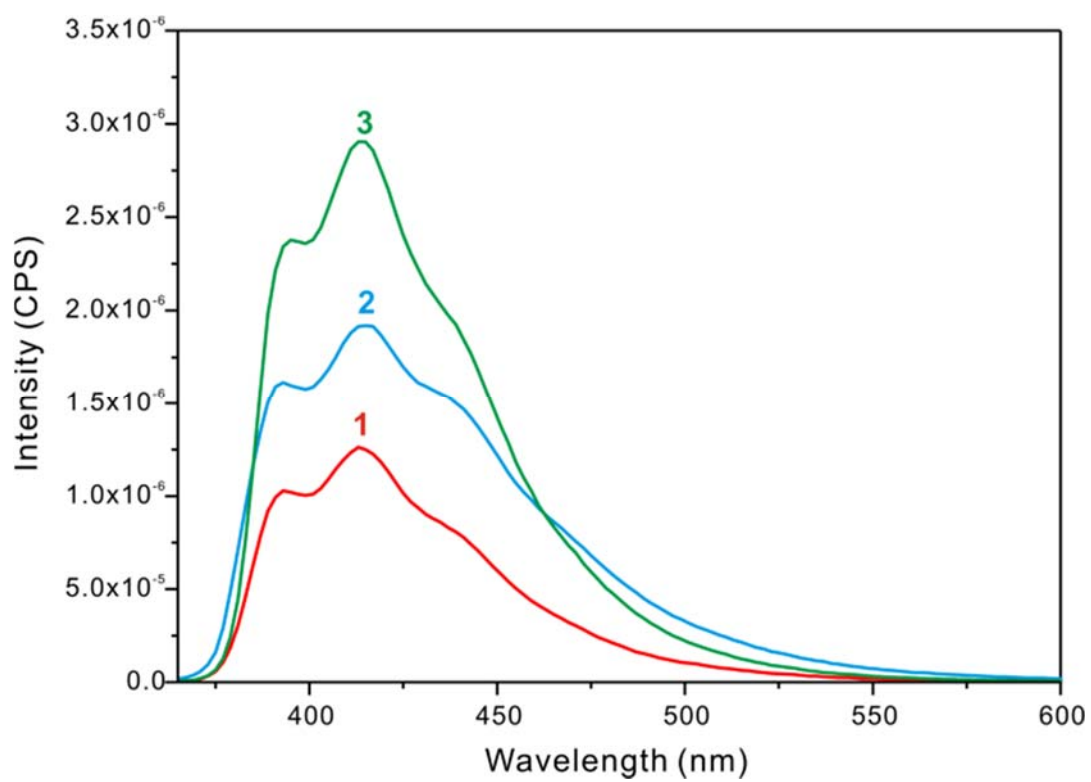
(d)

**Figure S9.**  $^1H$  NMR spectrum of (a) **3**, (b) **4**, (c) **5**, and (d) **4'** and in DMSO- $d_6$  with a small drop of  $HNO_3$  to dissolve the crystals. The humps around 4.5-5.5 ppm is due to the protonated water (\*:DEF).





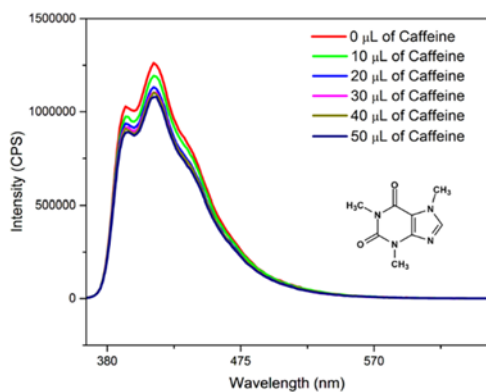
**Figure S10.** Solid-state emission spectra of bpeb, 3, 4, and 5 at room temperature (excitation at 360 nm).



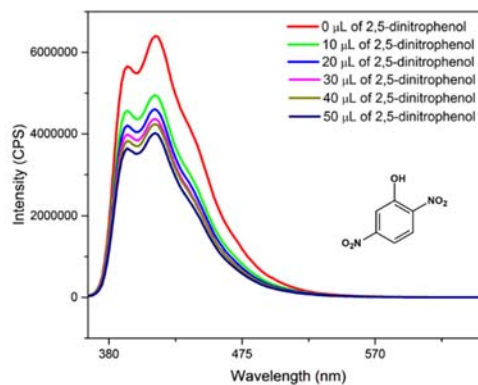
**Figure S11.** The PL spectra of 1-3 dispersed in 1 mL of DMF and excited at 360 nm.

**Sensing of nitro compounds and drug molecules with compounds 1-5:** Here we presented the PL titration data for the selected analytes which showed significant quenching behavior.

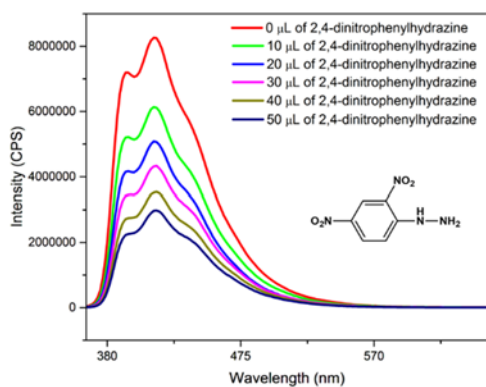
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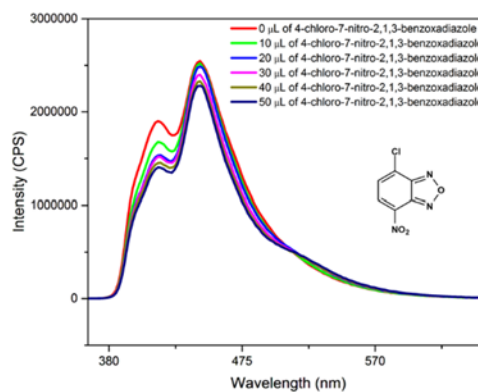
(a)



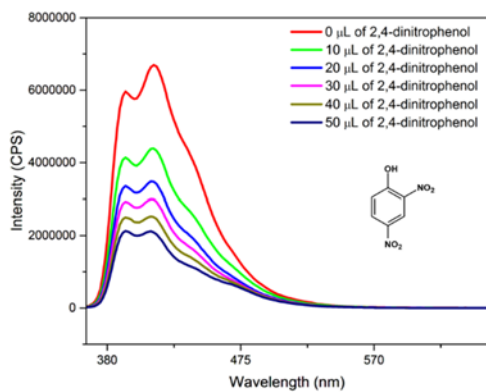
(b)



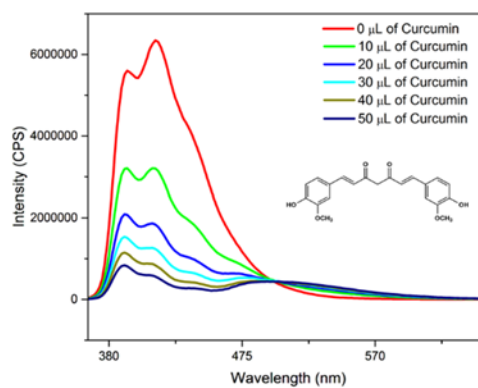
(c)



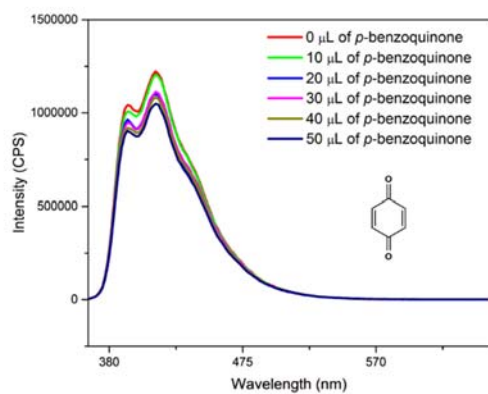
(d)



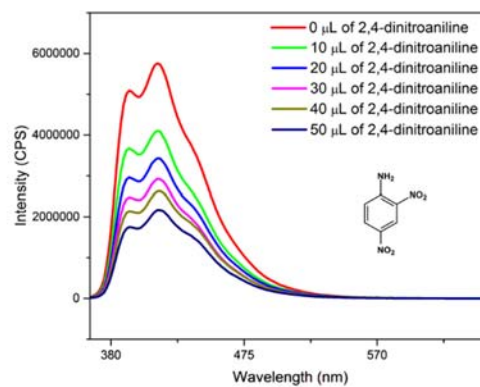
(e)



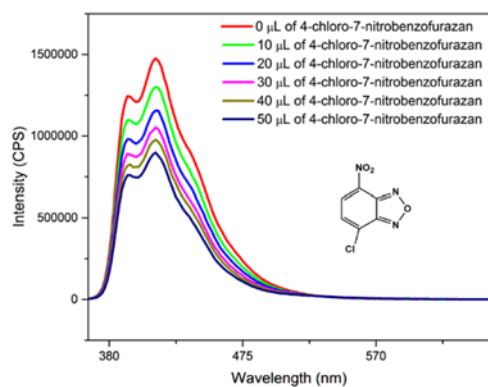
(f)



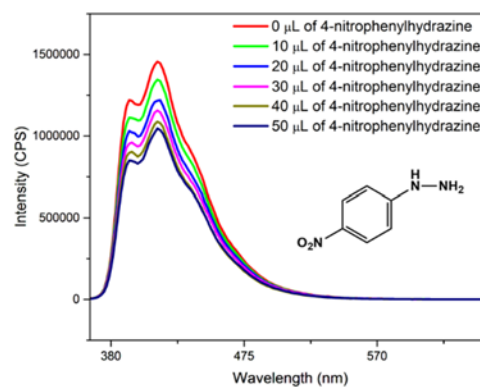
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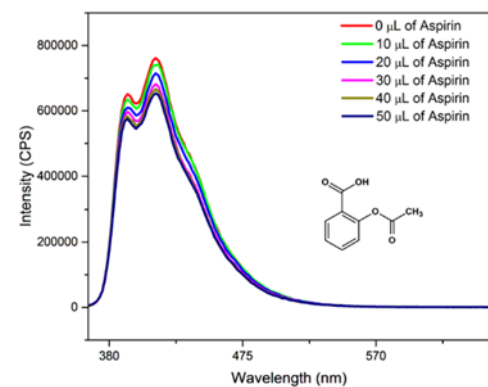
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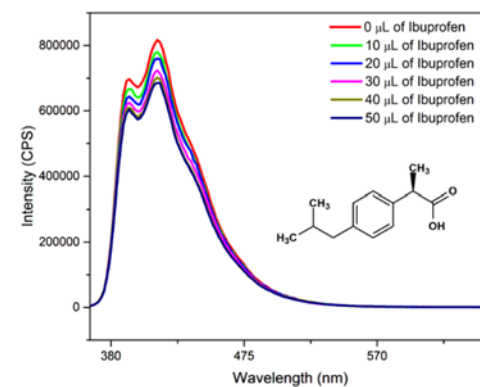
(i)



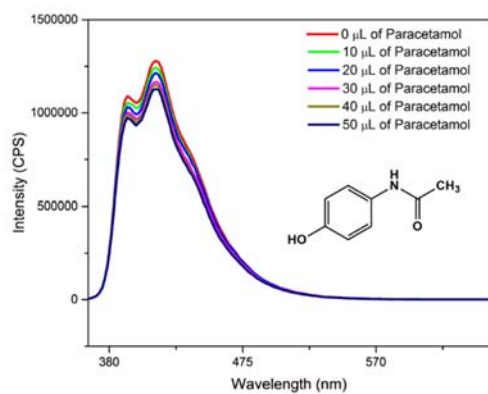
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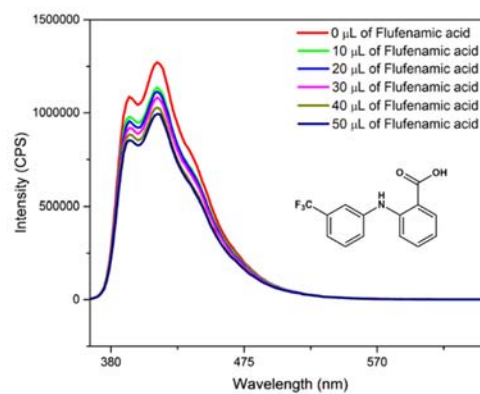
(k)



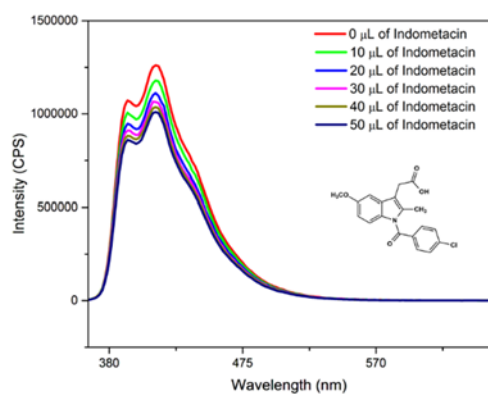
(l)



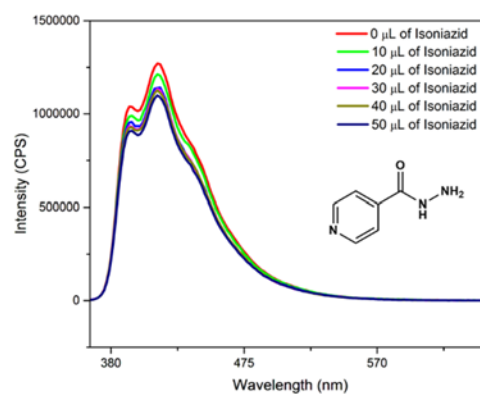
(m)



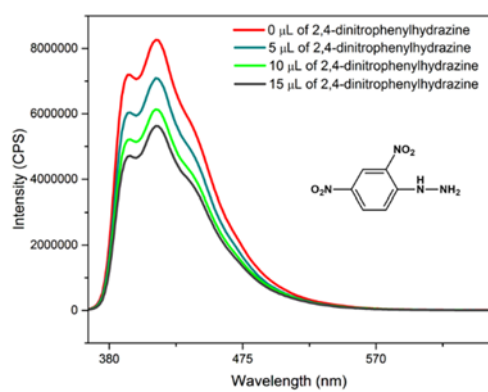
(n)



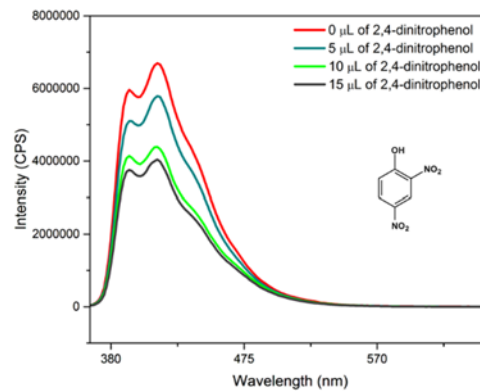
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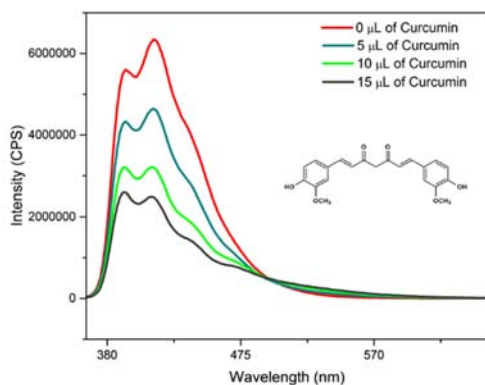
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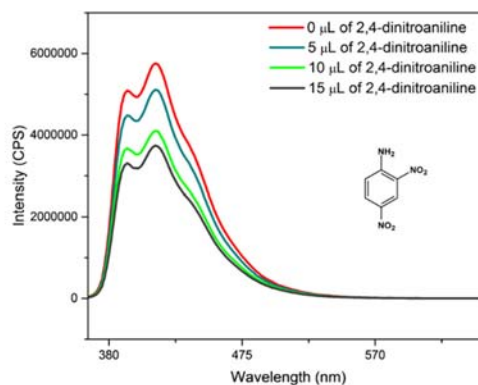
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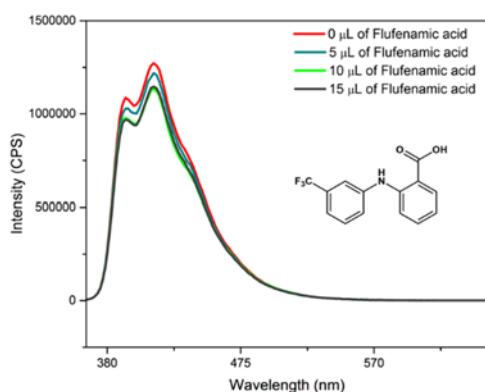
(r)



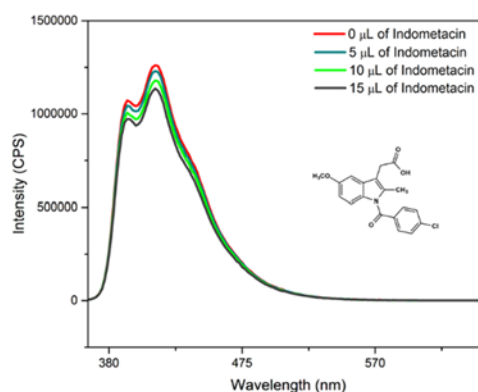
(s)



(t)



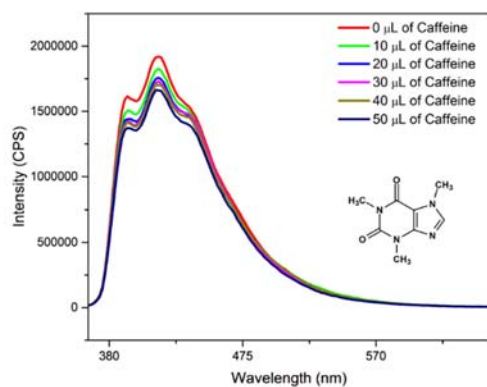
(u)



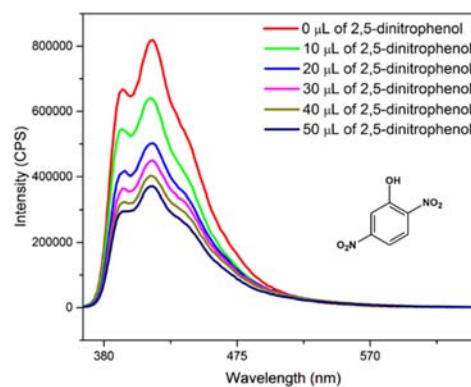
(v)

**Figure S12.** PL spectral changes of compound **1** dispersed in DMF with (a) caffeine, (b) 2,5-dinitrophenol, (c) 2,4-dinitrophenylhydrazine, (d) 4-chloro-7-nitro-2,1,3-benzoxadiazole, (e) 2,4-dinitrophenol, (f) curcumin, (g) *p*-benzoquinone, (h) 2,4-dinitroaniline, (i) 4-chloro-7-nitrobenzofurazan, (j) 4-nitrophenylhydrazine, (k) aspirin, (l) ibuprofen, (m) paracetamol, (n) flufenamic acid, (o) indometacin, (p) isoniazid, (q) 2,4-dinitrophenylhydrazine (LOD), (r) 2,4-dinitrophenol (LOD), (s) curcumin (LOD), (t) 2,4-dinitroaniline (LOD), (u) flufenamic acid (LOD), (v) indometacin.

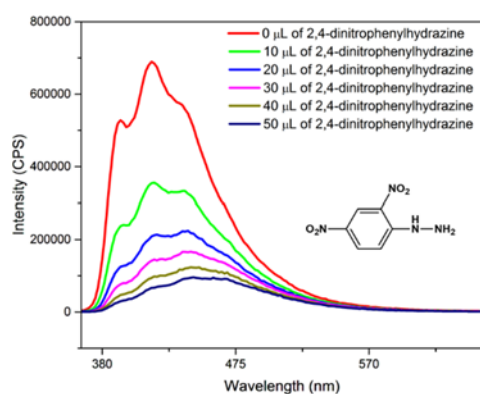
## Quenching data for compound 2:



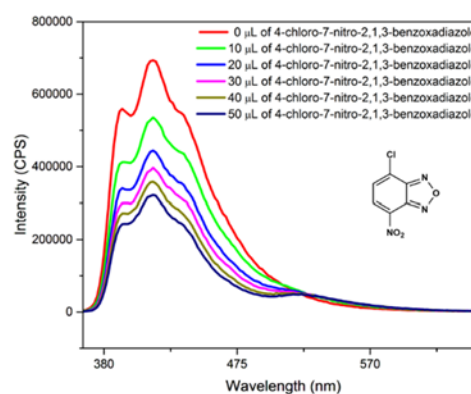
(a)



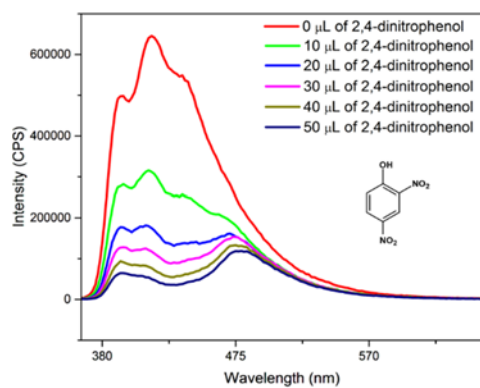
(b)



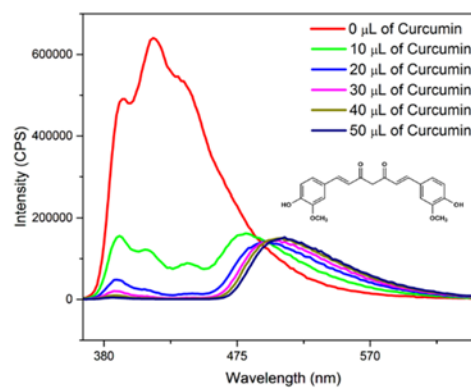
(c)



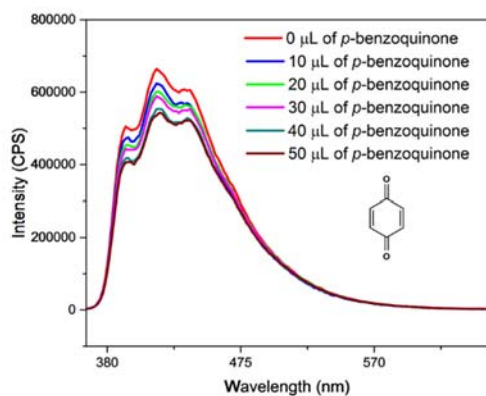
(d)



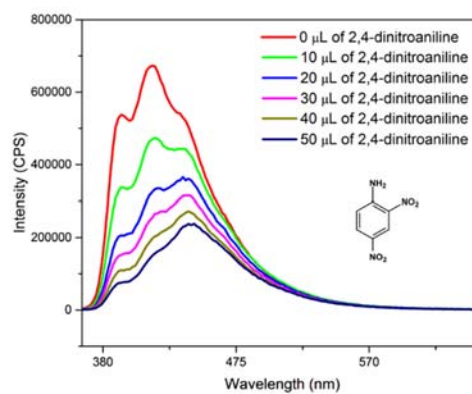
(e)



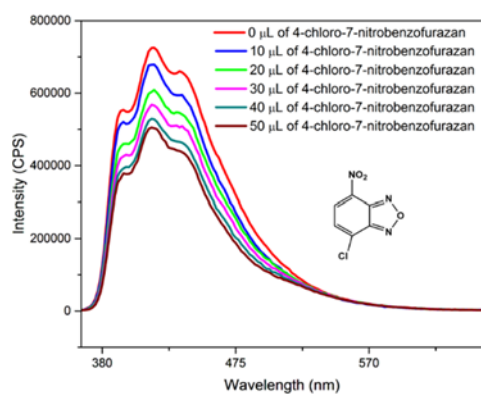
(f)



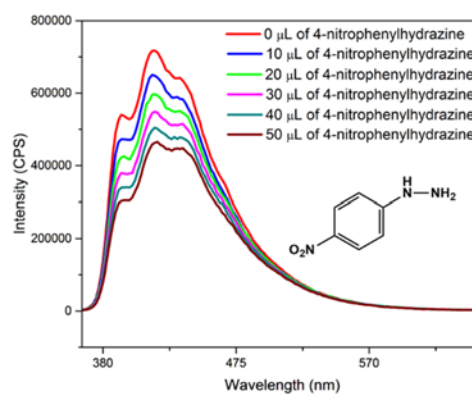
(g)



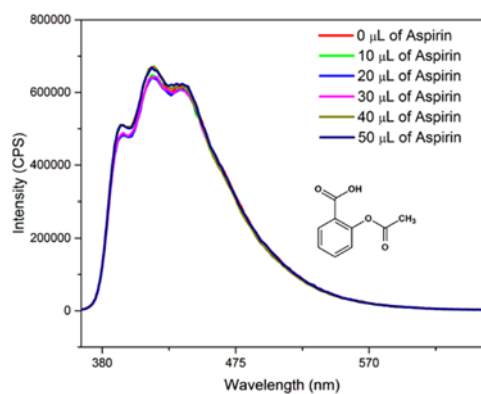
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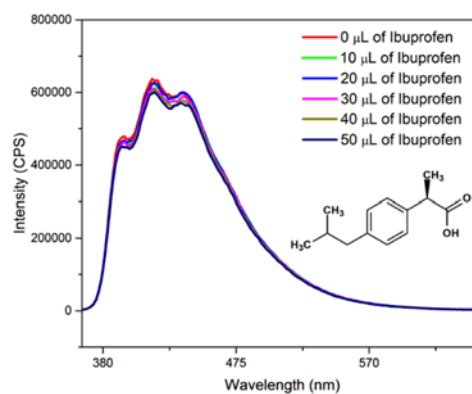
(i)



(j)

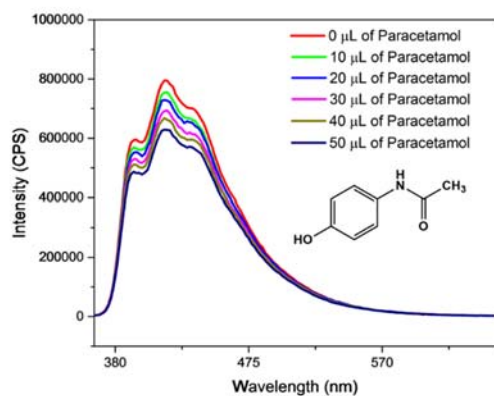


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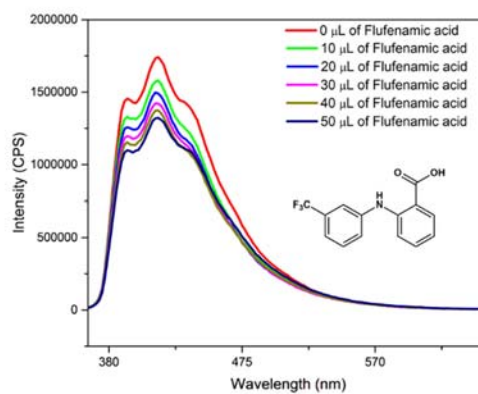


(l)

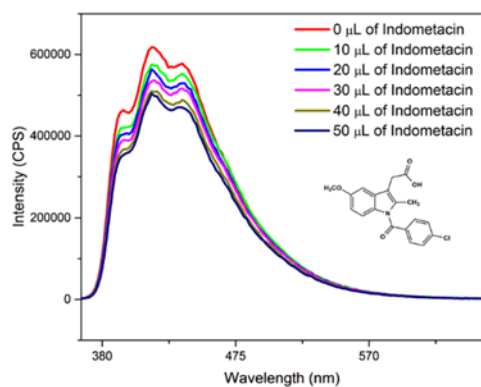




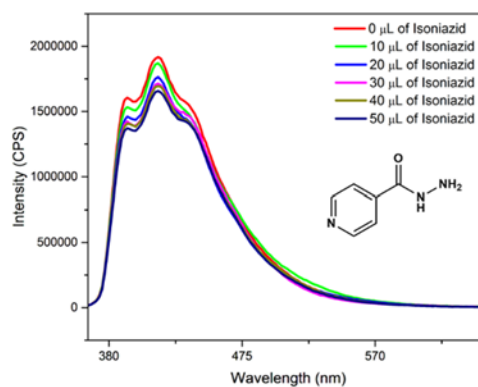
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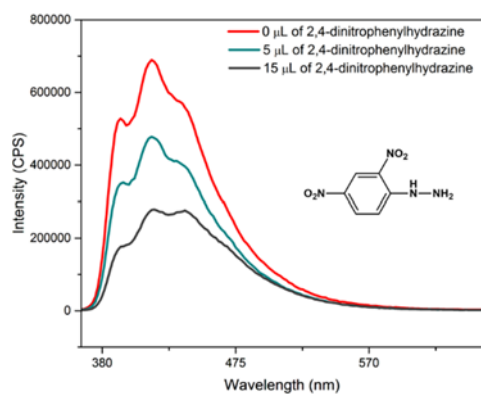
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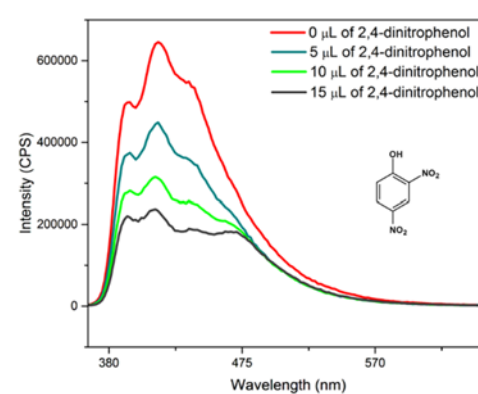
(o)



(p)

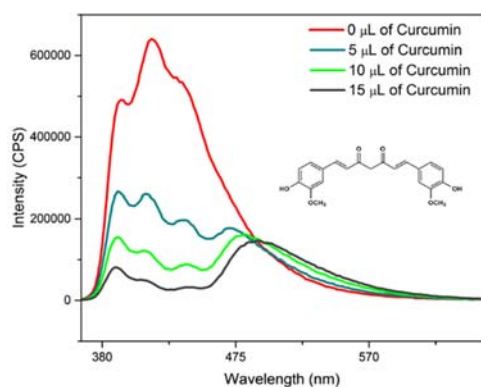


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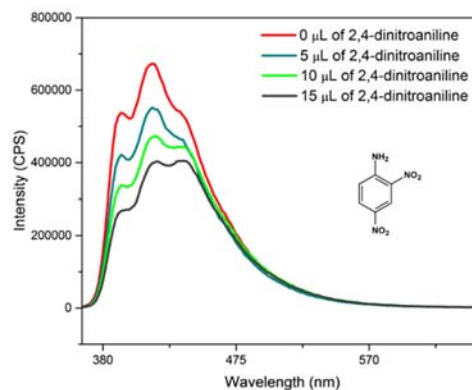


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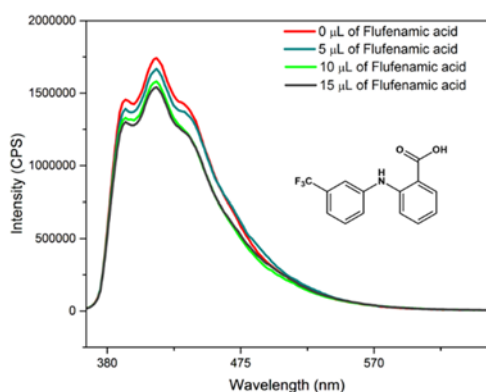




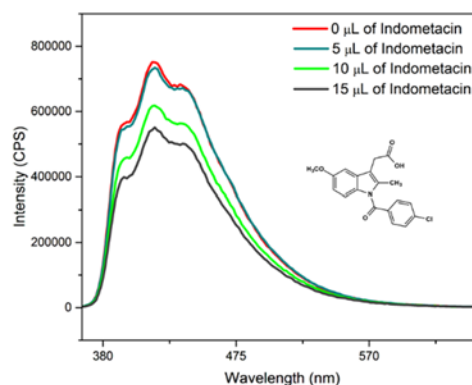
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(t)



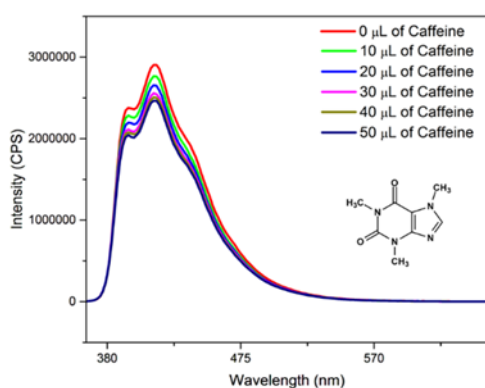
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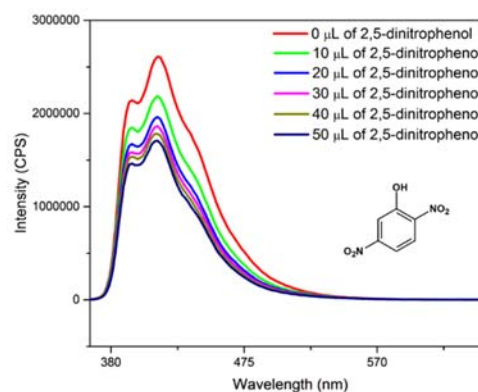
(v)

**Figure S13.** PL spectral changes of compound **2** dispersed in DMF with (a) caffeine, (b) 2,5-dinitrophenol, (c) 2,4-dinitrophenylhydrazine, (d) 4-chloro-7-nitro-2,1,3-benzoxadiazole, (e) 2,4-dinitrophenol, (f) curcumin, (g) *p*-benzoquinone, (h) 2,4-dinitroaniline, (i) 4-chloro-7-nitrobenzofurazan, (j) 4-nitrophenylhydrazine, (k) aspirin, (l) ibuprofen, (m) paracetamol, (n) flufenamic acid, (o) indometacin, (p) isoniazid, (q) 2,4-dinitrophenylhydrazine (LOD), (r) 2,4-dinitrophenol (LOD), (s) curcumin (LOD), (t) 2,4-dinitroaniline (LOD), (u) flufenamic acid (LOD), (v) indometacin.

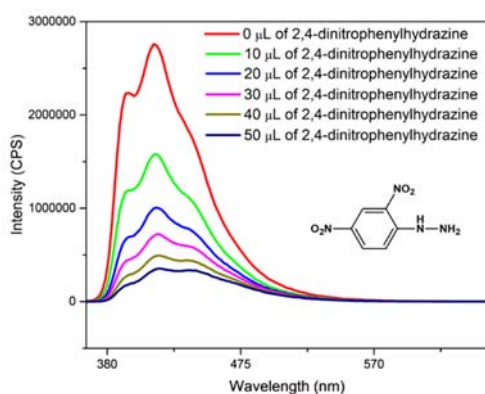
## Quenching data for compound 3:



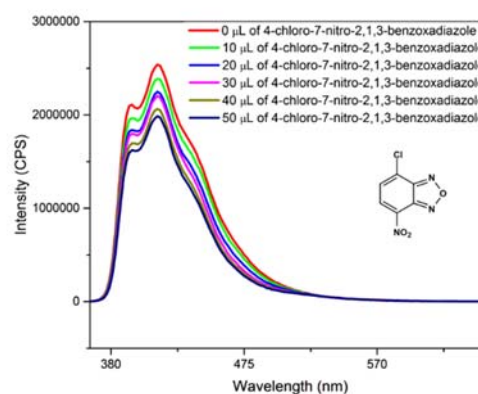
(a)



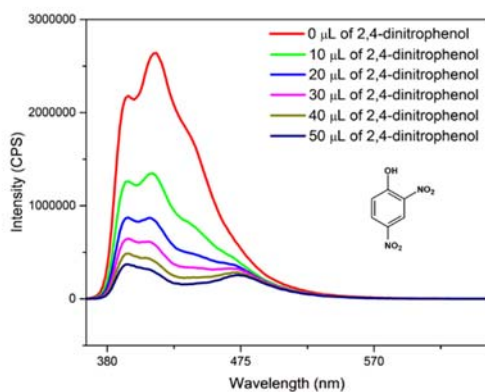
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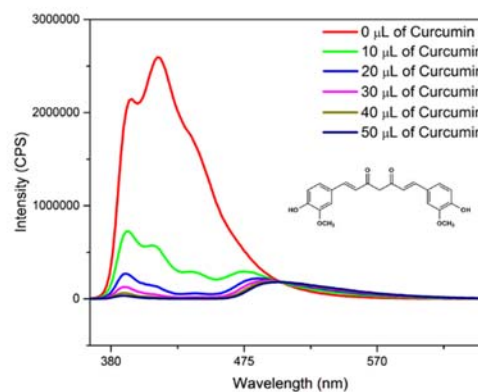
(c)



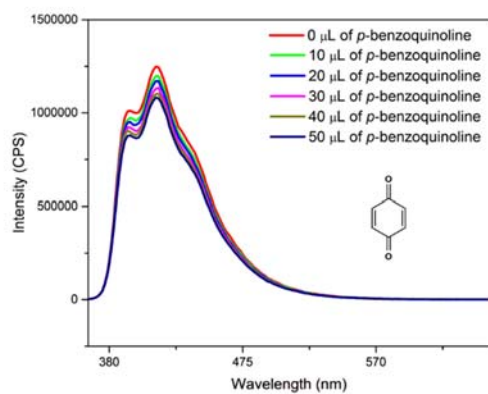
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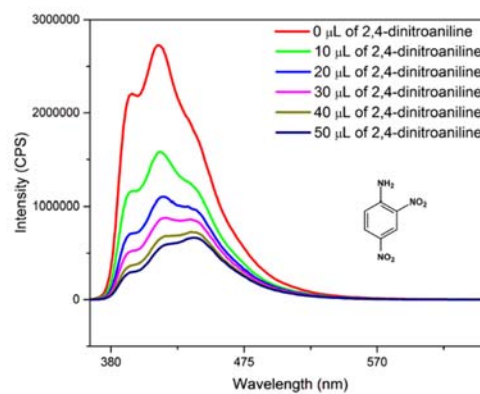
(e)



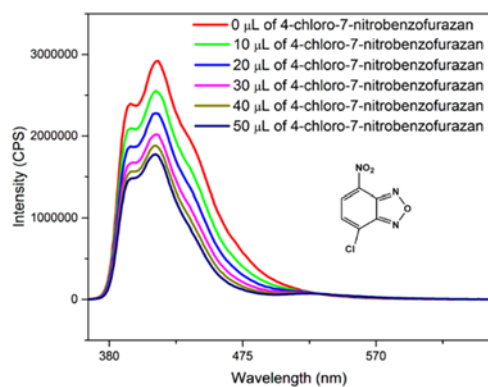
(f)



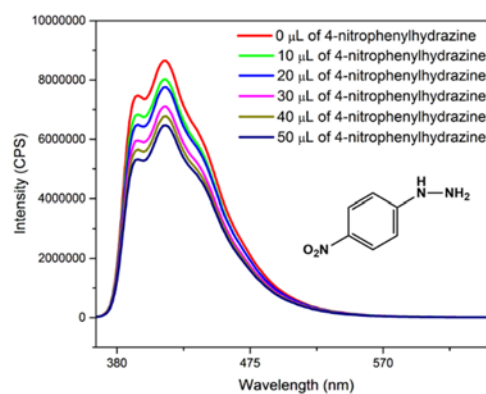
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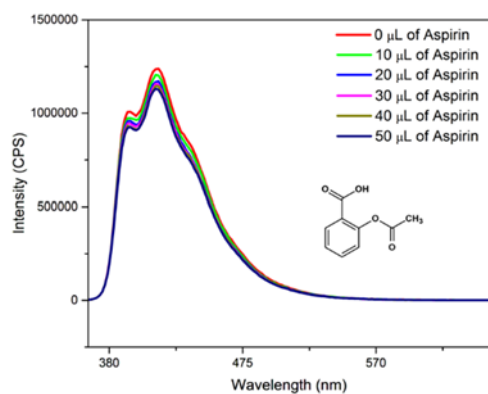
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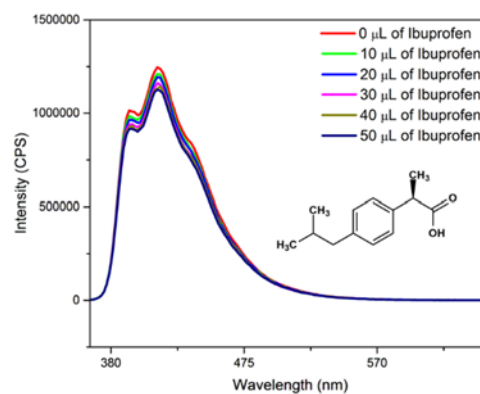
(i)



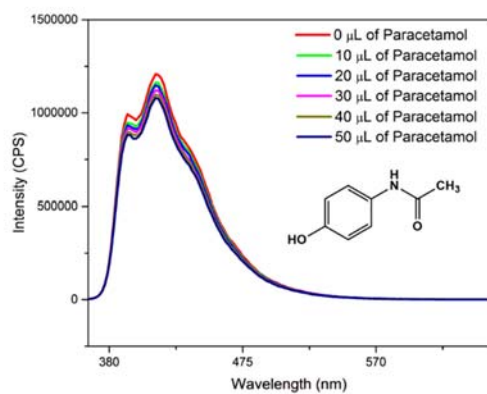
(j)



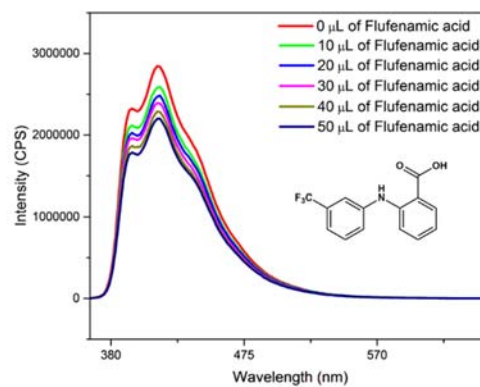
(k)



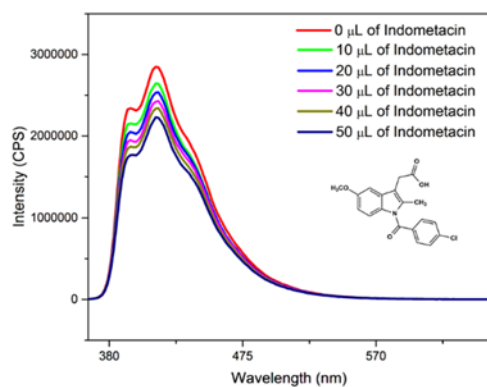
(l)



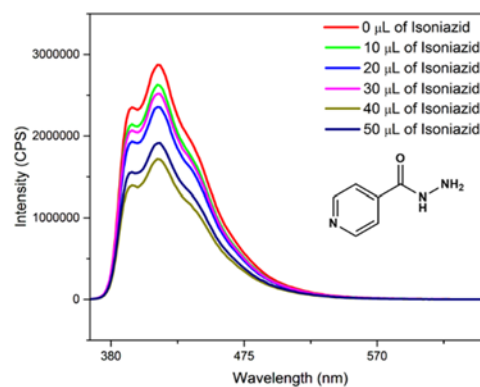
(m)



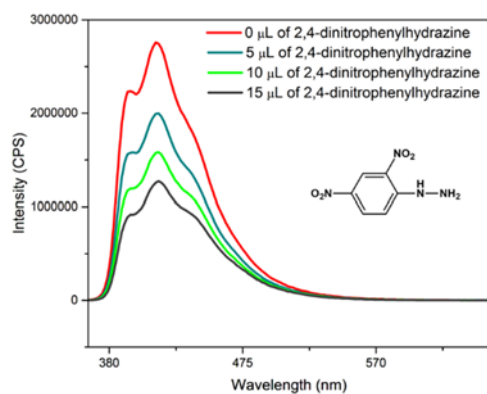
(n)



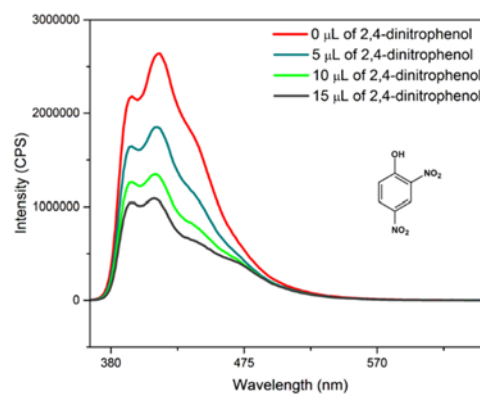
(o)



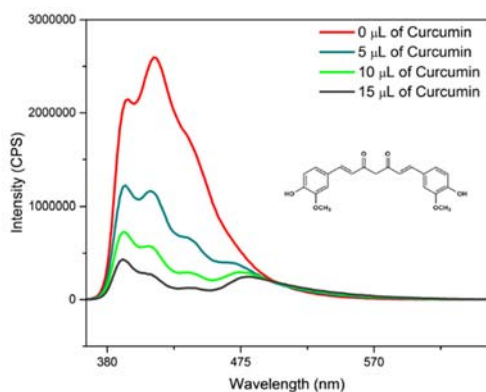
(p)



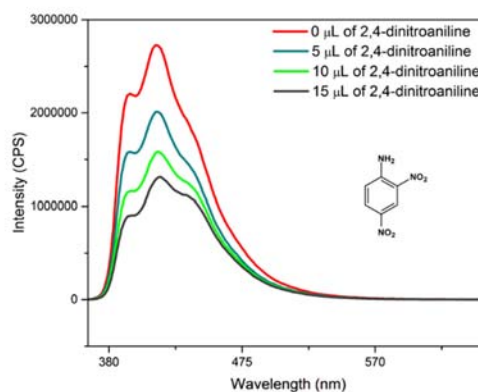
(q)



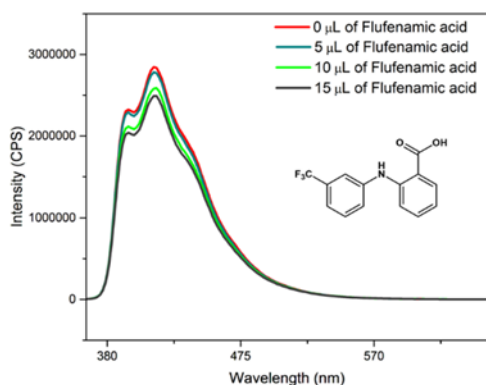
(r)



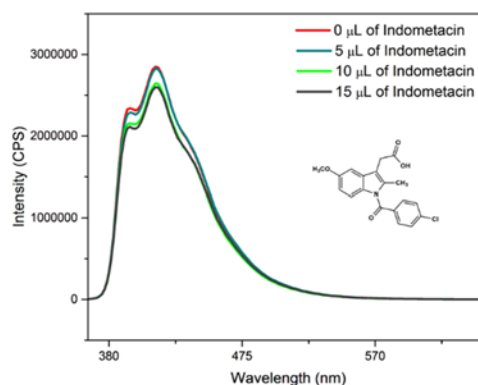
(s)



(t)



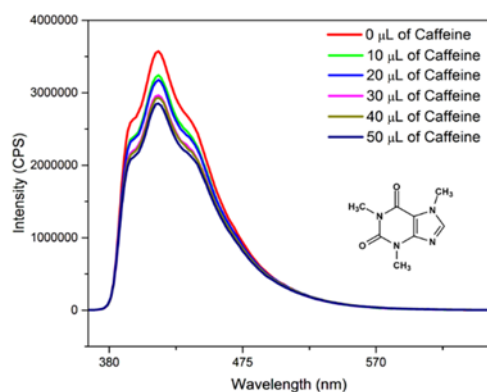
(u)



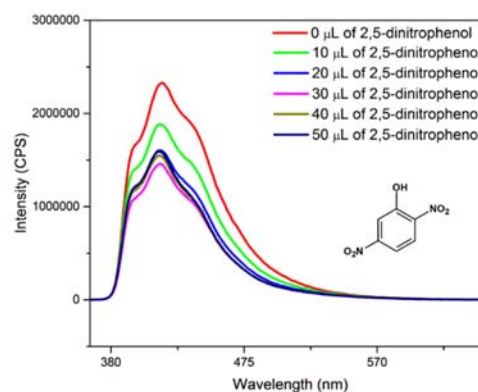
(v)

**Figure S14.** PL spectral changes of compound **3** dispersed in DMF with (a) caffeine, (b) 2,5-dinitrophenol, (c) 2,4-dinitrophenylhydrazine, (d) 4-chloro-7-nitro-2,1,3-benzoxadiazole, (e) 2,4-dinitrophenol, (f) curcumin, (g) *p*-benzoquinone, (h) 2,4-dinitroaniline, (i) 4-chloro-7-nitrobenzofurazan, (j) 4-nitrophenylhydrazine, (k) aspirin, (l) ibuprofen, (m) paracetamol, (n) flufenamic acid, (o) indometacin, (p) isoniazid, (q) 2,4-dinitrophenylhydrazine (LOD), (r) 2,4-dinitrophenol (LOD), (s) curcumin (LOD), (t) 2,4-dinitroaniline (LOD), (u) flufenamic acid (LOD), (v) indometacin.

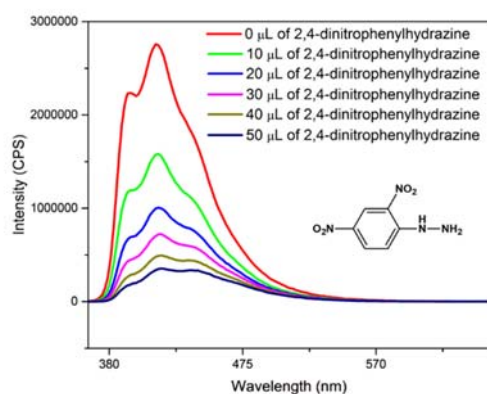
## Quenching data for compound 4:



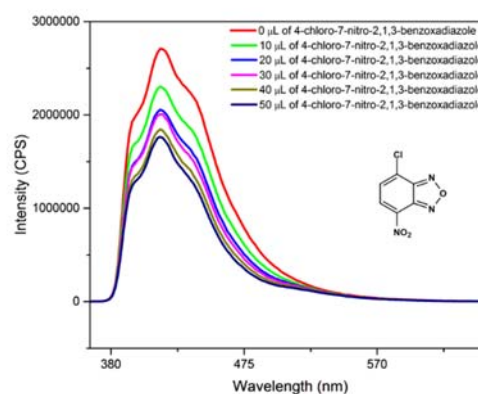
(a)



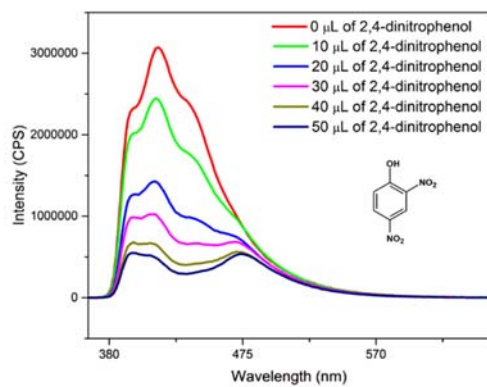
(b)



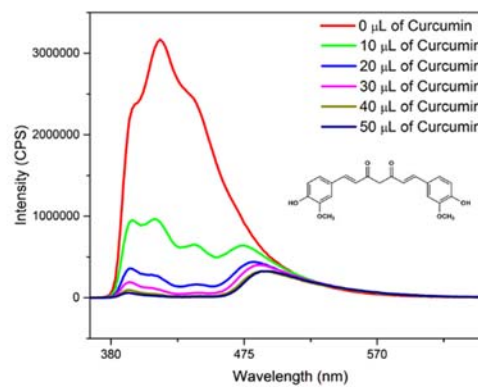
(c)



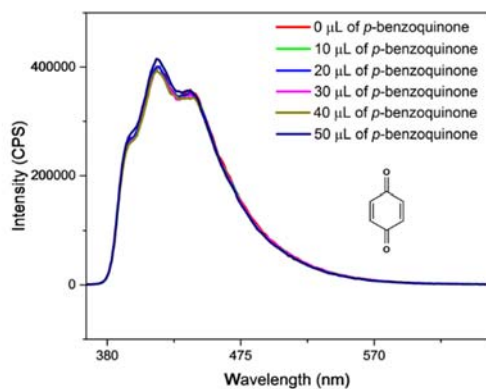
(d)



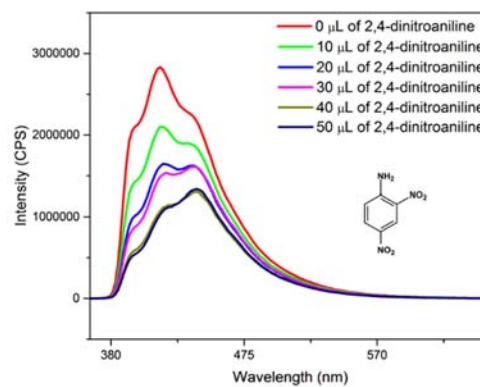
(e)



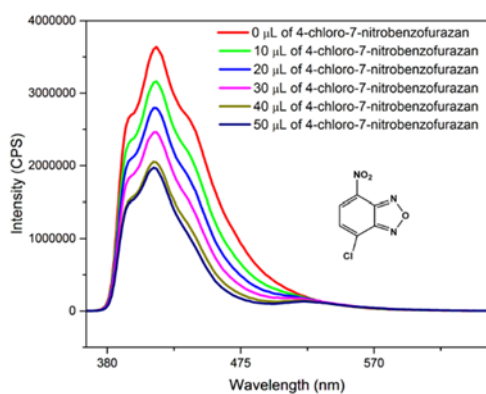
(f)



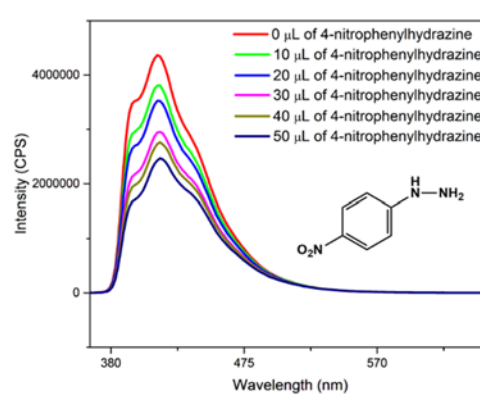
(g)



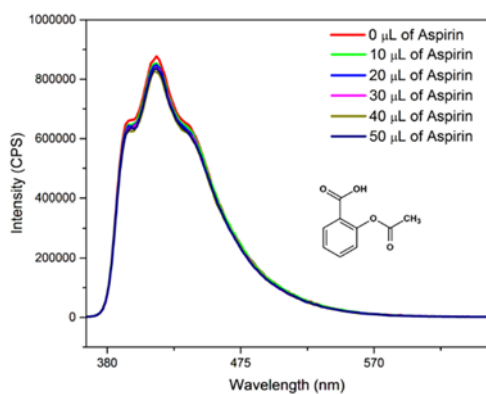
(h)



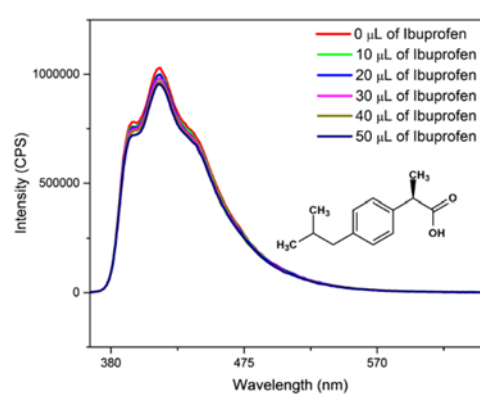
(i)



(j)

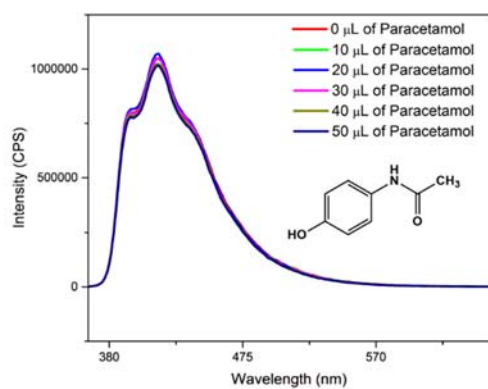


(k)

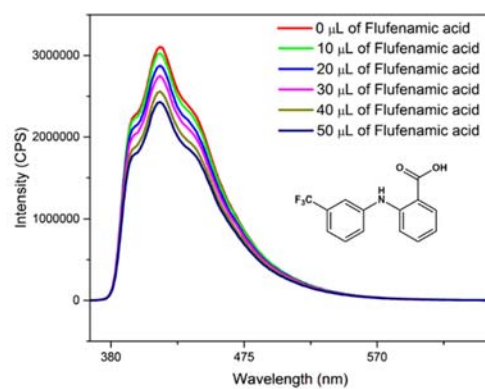


(l)

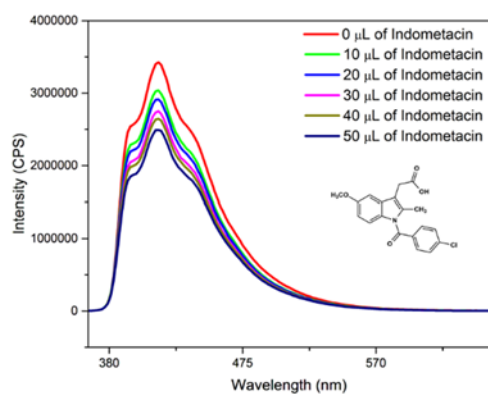




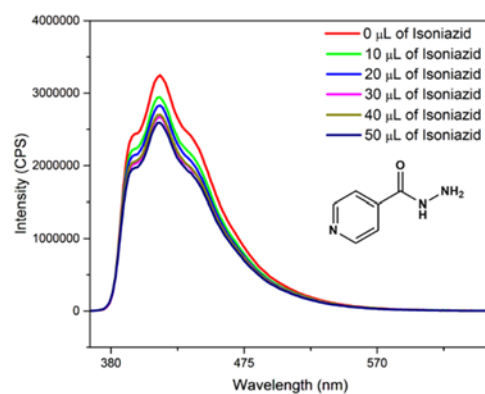
(m)



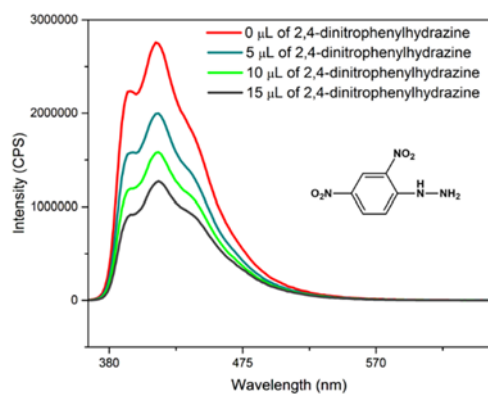
(n)



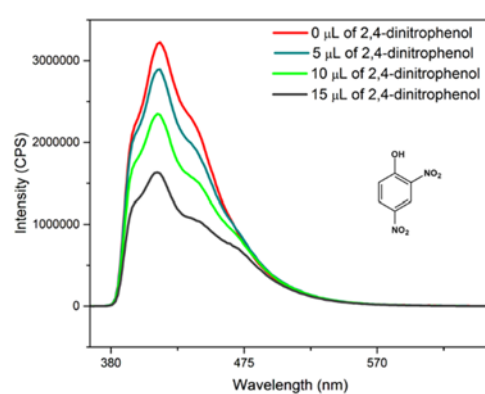
(o)



(p)

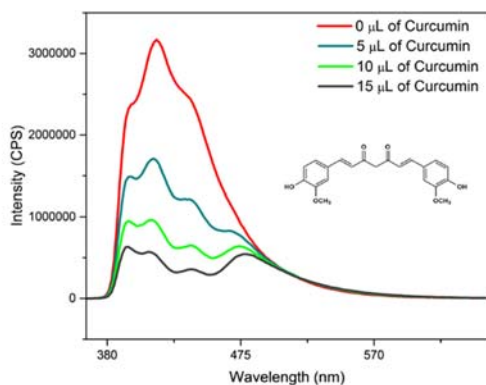


(q)

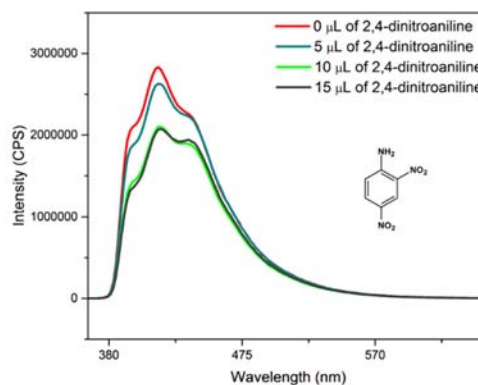


(r)

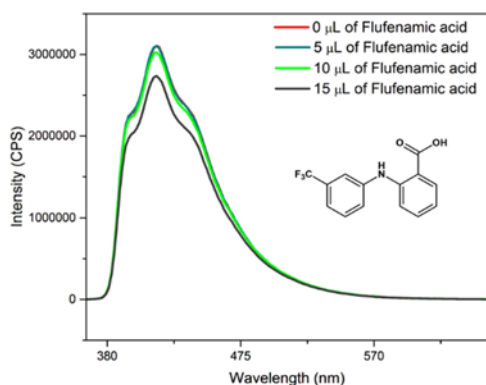




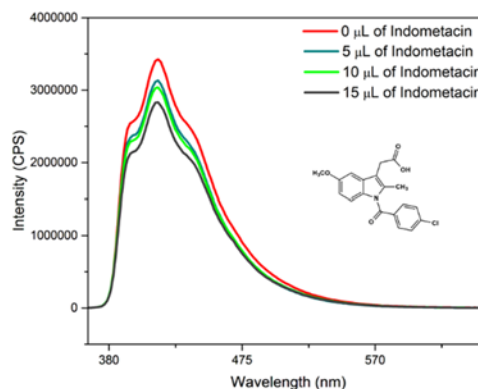
(s)



(t)



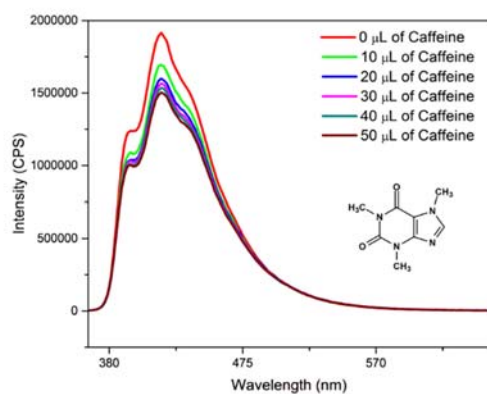
(u)



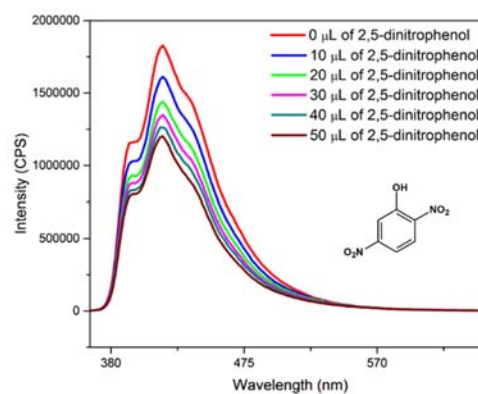
(v)

**Figure S15.** PL spectral changes of compound **4** dispersed in DMF with (a) caffeine, (b) 2,5-dinitrophenol, (c) 2,4-dinitrophenylhydrazine, (d) 4-chloro-7-nitro-2,1,3-benzoxadiazole, (e) 2,4-dinitrophenol, (f) curcumin, (g) *p*-benzoquinone, (h) 2,4-dinitroaniline, (i) 4-chloro-7-nitrobenzofurazan, (j) 4-nitrophenylhydrazine, (k) aspirin, (l) ibuprofen, (m) paracetamol, (n) flufenamic acid, (o) indometacin, (p) isoniazid, (q) 2,4-dinitrophenylhydrazine (LOD), (r) 2,4-dinitrophenol (LOD), (s) curcumin (LOD), (t) 2,4-dinitroaniline (LOD), (u) flufenamic acid (LOD), (v) indometacin.

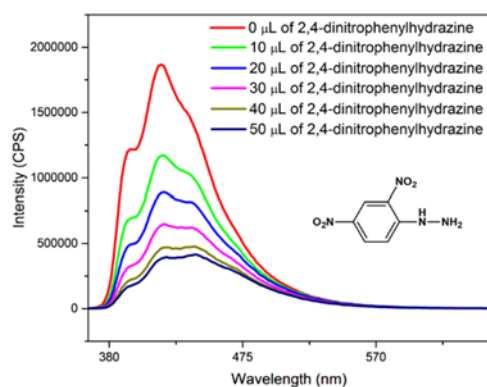
## Quenching data for compound 5:



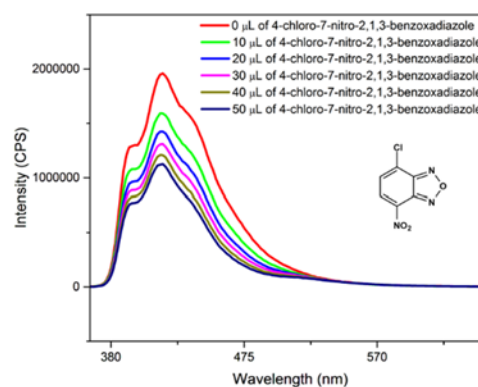
(a)



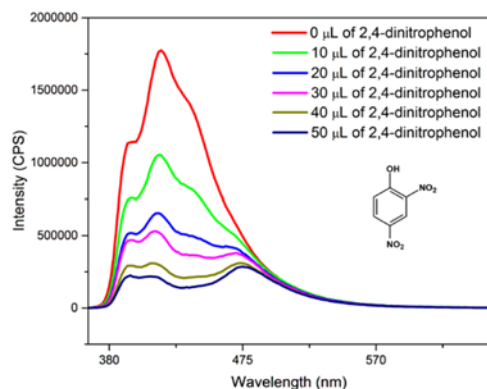
(b)



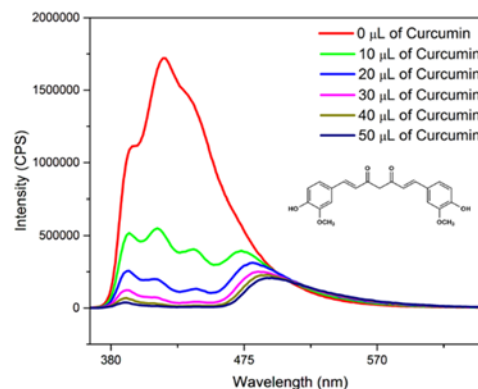
(c)



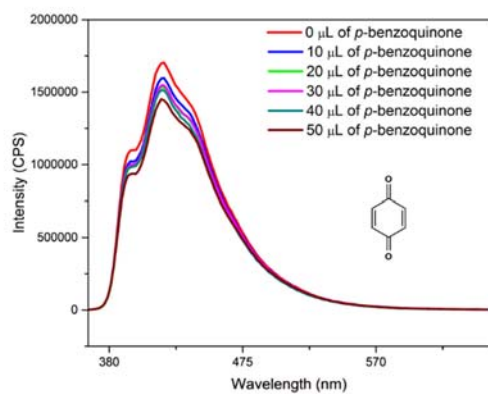
(d)



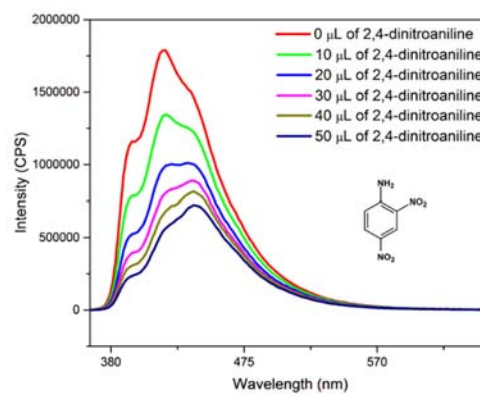
(e)



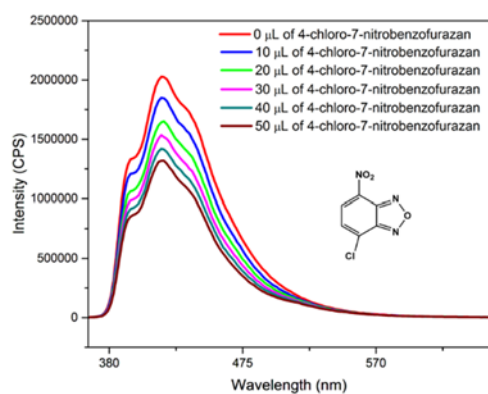
(f)



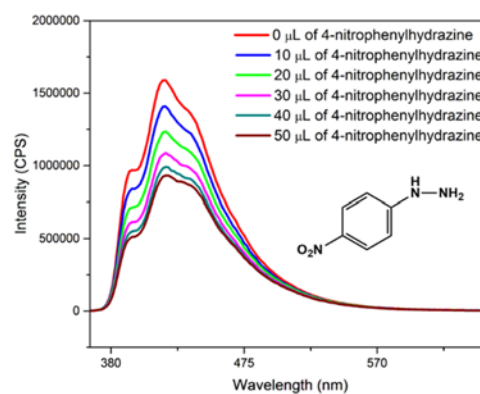
(g)



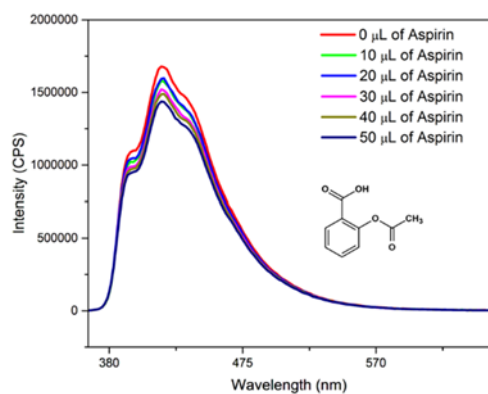
(h)



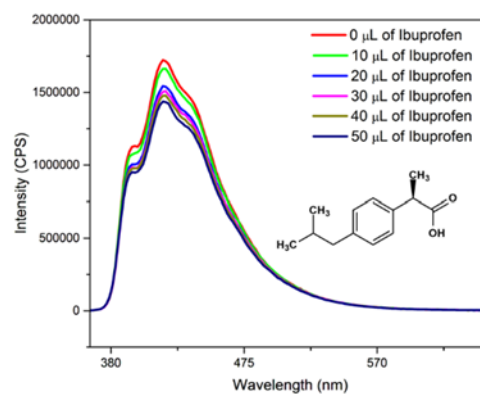
(i)



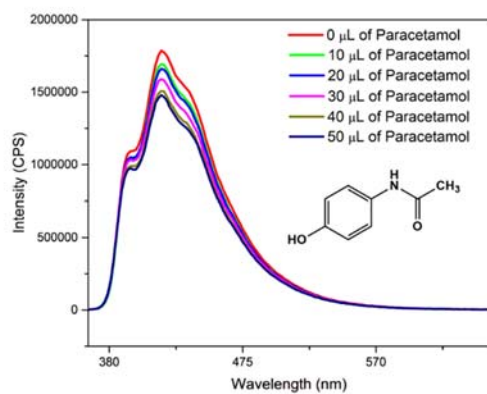
(j)



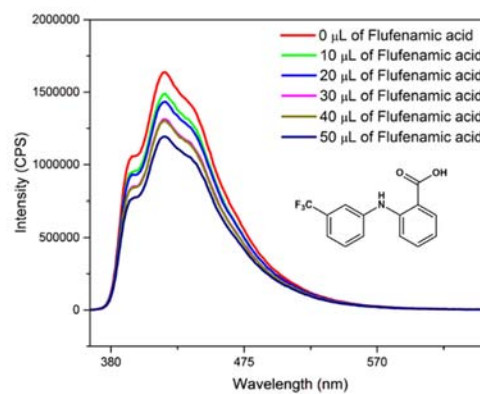
(k)



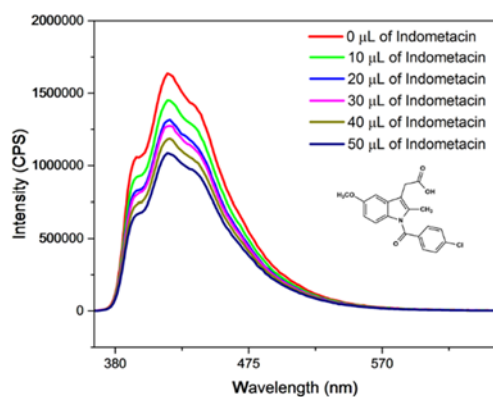
(l)



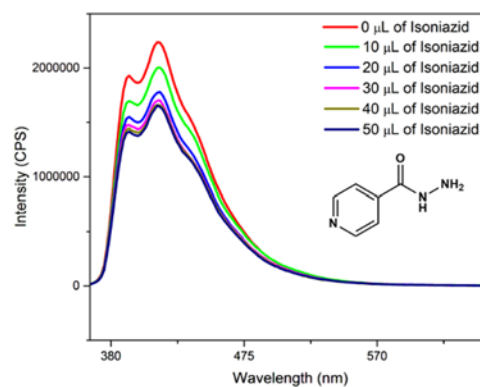
(m)



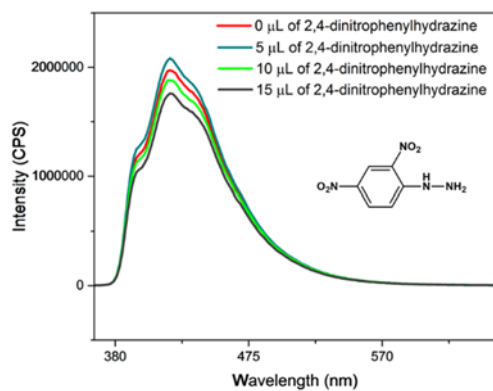
(n)



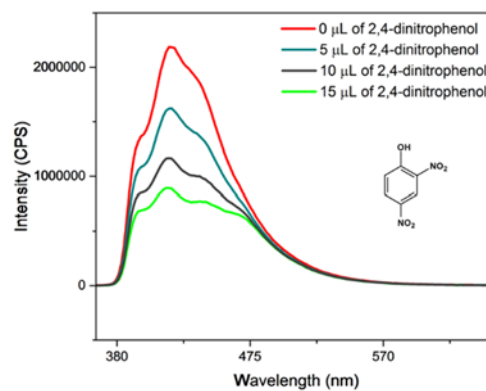
(o)



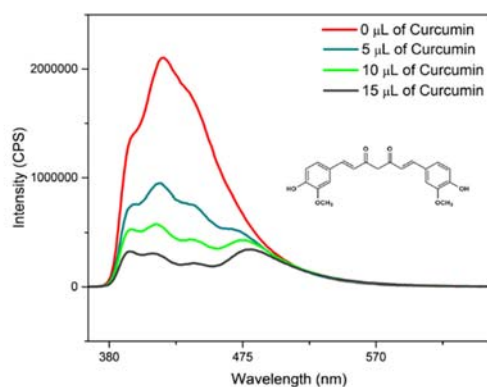
(p)



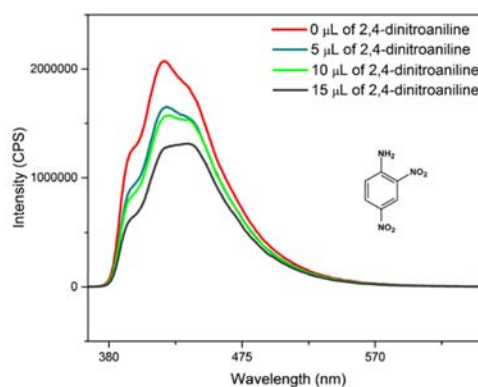
(q)



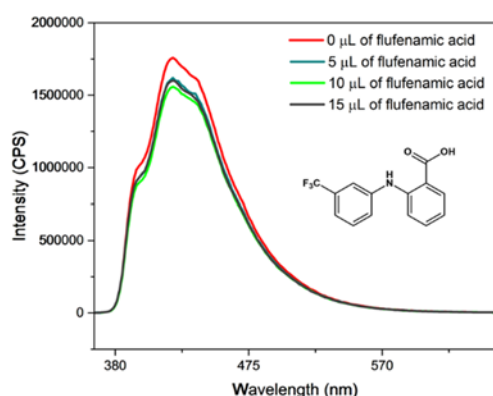
(r)



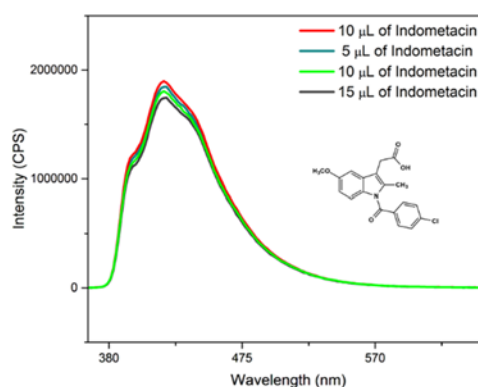
(s)



(t)

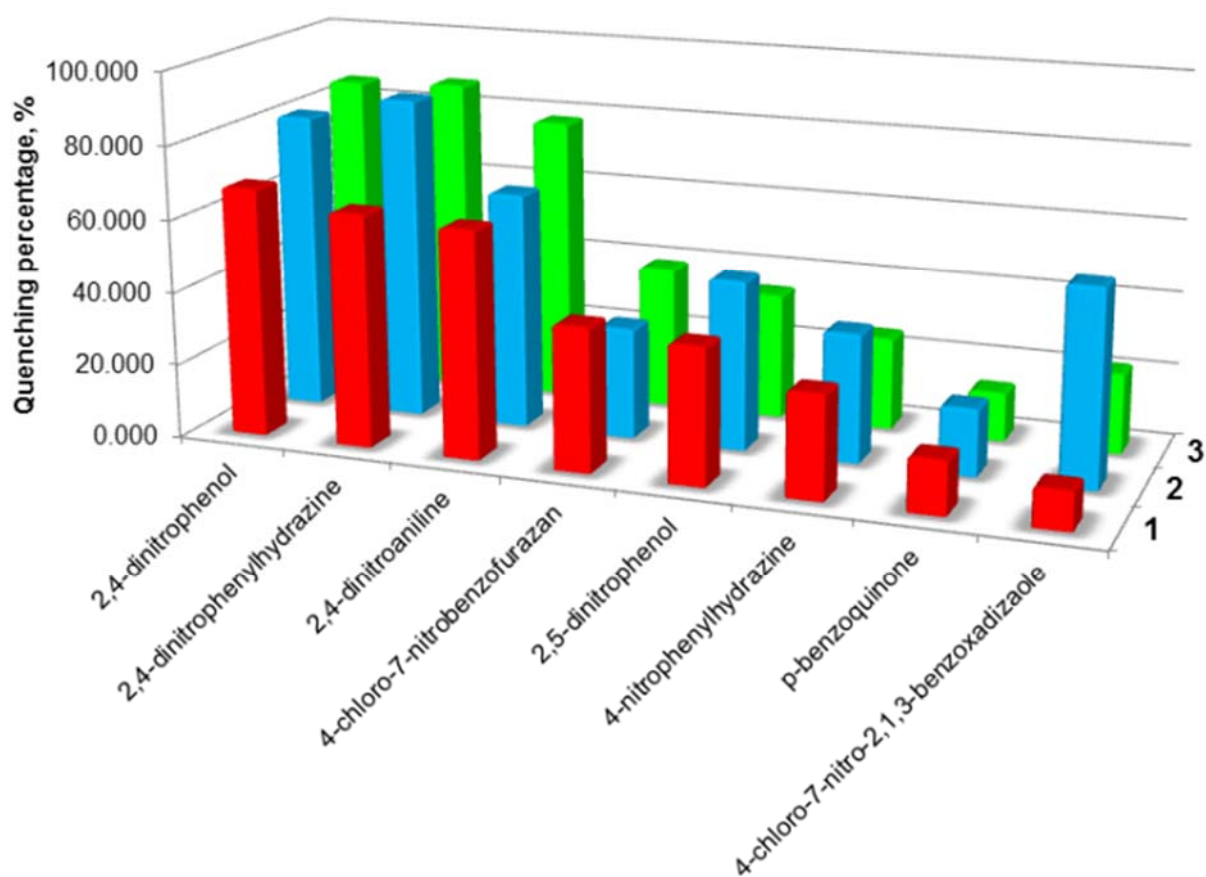


(u)

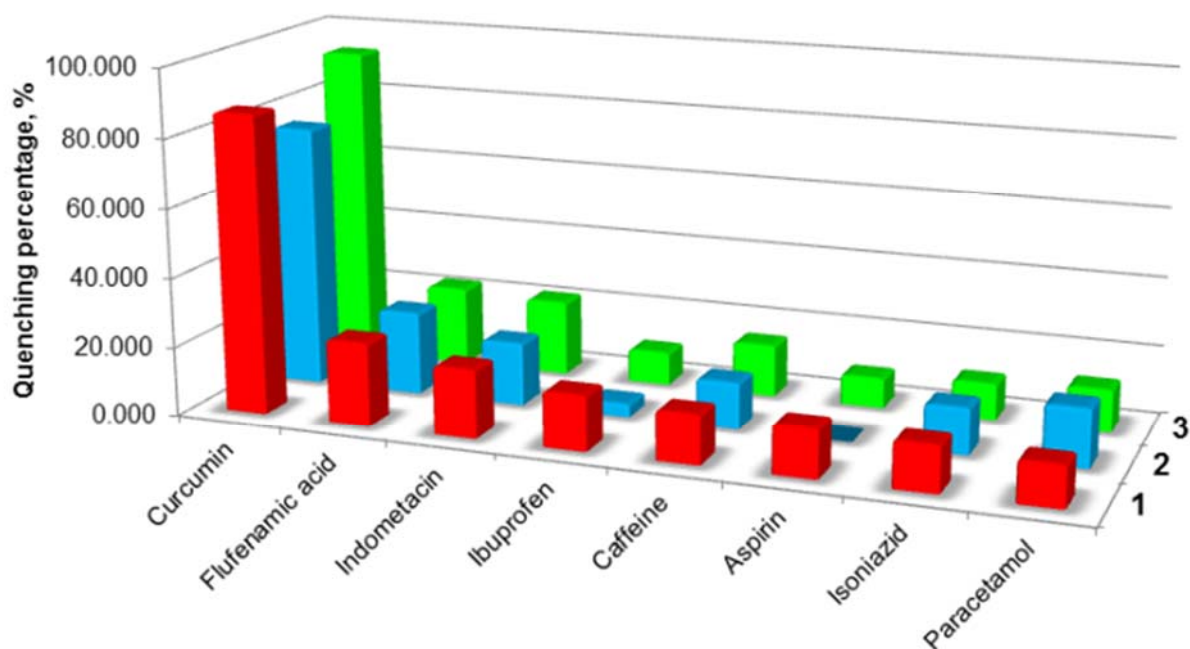


(v)

**Figure S16.** PL spectral changes of compound **5** dispersed in DMF with (a) caffeine, (b) 2,5-dinitrophenol, (c) 2,4-dinitrophenylhydrazine, (d) 4-chloro-7-nitro-2,1,3-benzoxadiazole, (e) 2,4-dinitrophenol, (f) curcumin, (g) *p*-benzoquinone, (h) 2,4-dinitroaniline, (i) 4-chloro-7-nitrobenzofurazan, (j) 4-nitrophenylhydrazine, (k) aspirin, (l) ibuprofen, (m) paracetamol, (n) flufenamic acid, (o) indometacin, (p) isoniazid, (q) 2,4-dinitrophenylhydrazine (LOD), (r) 2,4-dinitrophenol (LOD), (s) curcumin (LOD), (t) 2,4-dinitroaniline (LOD), (u) flufenamic acid (LOD), (v) indometacin.



(a)



(b)

**Figure S17.** PL quenching efficiencies obtained from (a) selected nitro analytes and (b) selected pharmaceutical drugs by 1-3.