# Electronic Supplementary Information (ESI)

# Supramolecular assemblies of Zn(II) complexes with D-π-A ligand for sensing specific organic molecules

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## EXPERIMENTAL

**X-ray crystallography.** Single-crystal X-ray diffraction data were collected on a Bruker D8 Venture diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The integration of diffraction data and intensity corrections for the Lorentz and polarization effects were performed by using SAINT program.[1] Semi-empirical absorption corrections were applied using SADABS program.[2] The structures were solved by direct methods with SHELXT-2014, expanded by subsequent Fourier-difference synthesis, and all the non-hydrogen atoms were refined anisotropically on $F^2$ using the full-matrix least-squares technique with the SHELXL-2018 crystallographic software package.[3,4] The free solvent molecules in the unit cell

have been taken into account by SQUEEZE option of the PLATON program.[5] The final chemical formulas were determined by volume/count electrons, elemental and TGA. The reported refinements are of the guest-free structures obtained by the SQUEEZE routine and the results were attached to the CIF files. The details of crystal parameters, data collection and refinements for **1**, **2** and **3** are listed in **Table 1**, and the selected bond lengths and angles are given in **Table S1**.

**Theoretical calculations.** First principle DFT calculations were carried out by using the Dmol3 module in Material Studio software package.[6] The initial configuration was fully optimized based on crystal structures of **1**, **2**, **3** and single molecular TNP by the Perdew-Burke-Ernzerhof (GGA-PBE) exchange correlation functional sets with spin-polarization, which is required to describe weak interactions.[7-9] The self-consistent field converged criterion was $1.0 \times 10^{-5}$ hartree atom$^{-1}$, and the converging criterion of structure optimization was $1.0 \times 10^{-3}$ hartree bohr$^{-1}$. The Brillouin zone was sampled by $1 \times 1 \times 1$ k-points, and test calculations reveal that the increase of k-points does not affect the results.

**Table S1** Selected bond lengths (Å) and angles (°) for **1**, **2** and **3**.

| | | | |
|---|---|---|---|
| | | **1** | |
| Zn(1)-N(4) | 2.220(3) | Zn(1)-N(5) | 2.071(2) |
| Zn(1)-N(6) | 2.188(3) | Zn(1)-N(7) | 2.212(2) |
| Zn(1)-N(8) | 2.082(2) | Zn(1)-N(9) | 2.168(2) |
| N(5)-Zn(1)-N(4) | 75.08(9) | N(5)-Zn(1)-N(6) | 76.03(9) |
| N(5)-Zn(1)-N(7) | 97.39(9) | N(5)-Zn(1)-N(8) | 172.54(9) |
| N(5)-Zn(1)-N(9) | 111.94(9) | N(6)-Zn(1)-N(7) | 94.79(9) |
| N(6)-Zn(1)-N(4) | 150.96(10) | N(7)-Zn(1)-N(4) | 91.71(9) |
| N(8)-Zn(1)-N(6) | 104.53(9) | N(8)-Zn(1)-N(7) | 75.16(9) |
| N(8)-Zn(1)-N(4) | 104.49(10) | N(8)-Zn(1)-N(9) | 75.49(9) |
| N(9)-Zn(1)-N(6) | 95.15(9) | N(9)-Zn(1)-N(7) | 150.51(9) |
| N(9)-Zn(1)-N(4) | 92.91(9) | | |
| | | **2** | |
| Zn(1)-O(4) | 1.962 (2) | Zn(1)-O(1) | 1.969(2) |
| Zn(1)-N(3) | 2.224(3) | Zn(1)-N(4) | 2.081(2) |
| Zn(1)-N(5) | 2.234(3) | | |
| O(4)-Zn(1)-O(1) | 120.78(9) | O(4)-Zn(1)-N(4) | 111.12(9) |
| O(4)-Zn(1)-N(5) | 96.83(9) | O(4)-Zn(1)-N(3) | 101.24(10) |
| O(1)-Zn(1)-N(4) | 128.09(9) | O(1)-Zn(1)-N(5) | 99.32(9) |
| O(1)-Zn(1)-N(3) | 93.84(10) | N(4)-Zn(1)-N(5) | 74.15(10) |
| N(4)-Zn(1)-N(3) | 74.76(10) | N(3)-Zn(1)-N(5) | 147.99(10) |
| | | **3** | |
| Zn(1)-O(4) | 1.9464(15) | Zn(1)-O(2) | 1.9585(15) |
| Zn(1)-N(3) | 2.1022(17) | Zn(1)-N(2) | 2.2086(18) |
| Zn(1)-N(4) | 2.2325(18) | | |
| O(4)-Zn(1)-O(2) | 120.05(6) | O(4)-Zn(1)-N(3) | 108.51(7) |
| O(4)-Zn(1)-N(2) | 103.98(7) | O(4)-Zn(1)-N(4) | 92.93(6) |
| O(2)-Zn(1)-N(3) | 131.43(6) | O(2)-Zn(1)-N(2) | 93.48(6) |
| O(2)-Zn(1)-N(4) | 101.92(7) | N(3)-Zn(1)-N(2) | 74.31(6) |
| N(3)-Zn(1)-N(4) | 73.98(6) | N(2)-Zn(1)-N(4) | 147.44(7) |

**Table S2** The member atoms of conjugate rings for **1**, **2** and **3**. (CgI = plane number I).

| | | | **1** | | | |
|---|---|---|---|---|---|---|
| CgI | Ring member atoms | | | | | |
| Cg1 | Zn1 | N4 | C19 | C18 | N5 | |
| Cg2 | Zn1 | N5 | C14 | C13 | N6 | |
| Cg3 | Zn1 | N7 | C28 | C29 | N8 | |
| Cg4 | Zn1 | N8 | C33 | C34 | N9 | |
| Cg5 | N1 | C47 | N3 | N2 | C48 | |
| Cg6 | N10 | N11 | C2 | N12 | C1 | |
| Cg7 | N4 | C19 | C20 | C21 | C22 | C23 |
| Cg8 | N5 | C14 | C15 | C16 | C17 | C18 |
| Cg9 | N6 | C9 | C10 | C11 | C12 | C13 |
| Cg10 | N7 | C24 | C25 | C26 | C27 | C28 |
| Cg11 | N8 | C29 | C30 | C31 | C32 | C33 |
| Cg12 | N9 | C34 | C35 | C36 | C37 | C38 |
| Cg13 | C3 | C4 | C5 | C6 | C7 | C8 |
| Cg14 | C39 | C40 | C41 | C42 | C43 | C44 |
| | | | **2** | | | |
| CgI | Ring member atoms | | | | | |
| Cg3 | Zn1A | O1 | C6 | O2 | | |
| Cg4 | Zn1 | N3 | C17 | C18 | N4 | |
| Cg5 | Zn1 | N4 | C22 | C23 | N5 | |
| Cg6 | N6 | C34 | N8 | N7 | C35 | |
| Cg7 | N1 | C1 | C2 | C3 | C4 | C5 |
| Cg8 | N2 | C10 | C9 | C8 | C12 | C11 |
| Cg9 | N3 | C13 | C14 | C15 | C16 | C17 |
| Cg10 | N4 | C18 | C19 | C20 | C21 | C22 |
| Cg11 | N5 | C23 | C24 | C25 | C26 | C27 |
| Cg12 | C28 | C29 | C30 | C31 | C32 | C33 |
| | | | **3** | | | |
| CgI | Ring member atoms | | | | | |
| Cg1 | Zn1 | N2 | C19 | C18 | N3 | |
| Cg2 | Zn1 | N3 | C11 | C12 | N4 | |
| Cg3 | N5 | N6 | C1 | N7 | C2 | |
| Cg4 | N1 | C28 | C27 | C26 | C30 | C29 |
| Cg5 | N2 | C19 | C20 | C21 | C22 | C23 |
| Cg6 | N3 | C11 | C10 | C9 | C17 | C18 |
| Cg7 | N4 | C12 | C13 | C14 | C15 | C16 |
| Cg8 | C3 | C4 | C5 | C6 | C7 | C8 |

**Table S3** The Cg-Cg distances (Å) between ring centroids for **1**, **2** and **3**.

| | | | | | |
|---|---|---|---|---|---|
| | | | **1** | | |
| | CgI->CgJ | Distance | | CgI->CgJ | Distance |
| 1 | Cg1->Cg7 #1 | 4.5638 (17) | 22 | Cg1->Cg10 #2 | 4.2112 (18) |
| 2 | Cg1->Cg12 #2 | 4.4870 (18) | 23 | Cg2->Cg10 #2 | 4.2163 (19) |
| 3 | Cg2->Cg12 #2 | 4.4927 (18) | 24 | Cg3->Cg5 #5 | 4.4197 (19) |
| 4 | Cg3->Cg7 #2 | 4.2965 (17) | 25 | Cg3->Cg9 #2 | 4.3678 (18) |
| 5 | Cg3->Cg12 #3 | 4.8883 (19) | 26 | Cg4->Cg6 #7 | 4.8967 (19) |
| 6 | Cg4->Cg7 #1 | 4.4145 (18) | 27 | Cg4->Cg9 #2 | 4.3979 (18) |
| 7 | Cg4->Cg10 #4 | 4.8897 (19) | 28 | Cg5->Cg3 #5 | 4.4196 (19) |
| 8 | Cg5->Cg10 #5 | 3.852 (2) | 29 | Cg5->Cg11 #6 | 4.9993 (19) |
| 9 | Cg5->Cg14 #6 | 3.723 (2) | 30 | Cg6->Cg4 #7 | 4.8967 (19) |
| 10 | Cg6->Cg12 #7 | 3.676 (2) | 31 | Cg6->Cg13 #9 | 3.803 (2) |
| 11 | Cg7->Cg1 #1 | 4.5637 (17) | 32 | Cg7->Cg7 #1 | 4.0946 (19) |
| 12 | Cg7->Cg8 #1 | 4.9034 (18) | 33 | Cg7->Cg12 #3 | 4.962 (2) |
| 13 | Cg8->Cg7 #1 | 4.9035 (18) | 34 | Cg9->Cg13 #8 | 4.927 (2) |
| 14 | Cg9->Cg13 #5 | 4.677 (2) | 35 | Cg10->Cg4 #3 | 4.8896 (19) |
| 15 | Cg10->Cg5 #5 | 3.852 (2) | 36 | Cg10->Cg12 #3 | 3.563 (2) |
| 16 | Cg10->Cg13 #5 | 4.374 (2) | 37 | Cg11->Cg5 #9 | 4.9995 (19) |
| 17 | Cg12->Cg3 #4 | 4.8884 (19) | 38 | Cg12->Cg6 #7 | 3.676 (2) |
| 18 | Cg12->Cg10 #4 | 3.563 (2) | 39 | Cg13->Cg6 #6 | 3.803 (2) |
| 19 | Cg13->Cg9 #8 | 4.927 (2) | 40 | Cg13->Cg10 #5 | 4.374 (2) |
| 20 | Cg13->Cg14 #6 | 4.793 (2) | 41 | Cg14->Cg5 #9 | 3.723 (2) |
| 21 | Cg14->Cg13 #9 | 4.793 (2) | | | |
| | | | **2** | | |
| | CgI->CgJ | Distance | | CgI->CgJ | Distance |
| 1 | Cg3->Cg10 #1 | 4.957 (3) | 13 | Cg7->Cg12 #1 | 4.507 (2) |
| 2 | Cg3->Cg11 #1 | 4.856 (3) | 14 | Cg8->Cg9 #2 | 4.764 (2) |
| 3 | Cg6->Cg7 #3 | 4.211 (2) | 15 | Cg9->Cg8 #4 | 4.944 (2) |
| 4 | Cg7->Cg6 #5 | 4.211 (2) | 16 | Cg10->Cg3 #1 | 4.957 (3) |
| 5 | Cg8->Cg9 #6 | 4.944 (2) | 17 | Cg11->Cg3 #1 | 4.856 (3) |
| 6 | Cg9->Cg7 #7 | 4.905 (2) | 18 | Cg11->Cg6 #6 | 4.821 (2) |
| 7 | Cg9->Cg8 #2 | 4.764 (2) | 19 | Cg11->Cg10 #1 | 3.7287 (19) |

| | | | | | |
|---|---|---|---|---|---|
| 8 | Cg10->Cg11 #1 | 3.7285 (19) | 20 | Cg11->Cg11 #1 | 4.491 (2) |
| 9 | Cg11->Cg4 #1 | 3.8523 (18) | 21 | Cg11->Cg10 #6 | 3.6942 (19) |
| 10 | Cg3->Cg11 #8 | 4.270 (3) | 22 | Cg12->Cg7 #1 | 4.507 (2) |
| 11 | Cg4->Cg11 #1 | 3.8523 (18) | 23 | Cg12->Cg11 #4 | 3.6943 (19) |
| 12 | Cg6->Cg11 #4 | 4.821 (2) | | | |

**3**

| | CgI->CgJ | Distance | | CgI->CgJ | Distance |
|---|---|---|---|---|---|
| 1 | Cg1->Cg7 #1 | 3.8704 (12) | 12 | Cg5->Cg4 #8 | 4.9432 (12) |
| 2 | Cg2->Cg7 #1 | 3.4880 (12) | 13 | Cg6->Cg7 #1 | 3.8434 (12) |
| 3 | Cg3->Cg3 #2 | 3.8092 (18) | 14 | Cg7->Cg2 #1 | 3.4880 (12) |
| 4 | Cg3->Cg7 #3 | 4.9161 (14) | 15 | Cg7->Cg3 #5 | 4.9161 (14) |
| 5 | Cg4->Cg8 #1 | 4.5293 (13) | 16 | Cg7->Cg6 #1 | 3.8434 (12) |
| 6 | Cg5->Cg8 #4 | 3.6999 (13) | 17 | Cg7->Cg7 #1 | 4.4205 (12) |
| 7 | Cg7->Cg1 #1 | 3.8705 (12) | 18 | Cg7->Cg8 #5 | 3.6631 (12) |
| 8 | Cg2->Cg2 #1 | 3.9608 (12) | 19 | Cg8->Cg2 #3 | 4.8088 (11) |
| 9 | Cg2->Cg8 #5 | 4.8087 (11) | 20 | Cg8->Cg5 #4 | 3.6999 (13) |
| 10 | Cg3->Cg4 #6 | 4.2854 (16) | 21 | Cg8->Cg7 #3 | 3.6632 (12) |
| 11 | Cg4->Cg3 #7 | 4.2854 (16) | | | |

Symmetry codes: #1 1-x,-y,1-z; #2 x,y,z; #3 1+x,y,z; #4 -1+x,y,z; #5 1-x,1-y,1-z; #6 x,y,1+z; #7 1-x,-y,-z; #8 -x,1-y,1-z; #9 x,y,-1+z for **1**; #1 -x,1-y,1-z; #2 -x,1-y,-z; #3 1+x,1+y,z; #4 1+x,y,z; #5 -1+x,-1+y,z; #6 -1+x,y,z; #7 -x,-y,1-z; #8 x,y,z for **2**; #1 2-x,1-y,1-z; #2 -x,2-y,-z; #3 -1+x,y,z; #4 1-x,2-y,1-z ;#5 1+x,y,z; #6 -1+x,y,-1+z; #7 1+x,y,1+z; #8 2-x,1-y,2-z for **3**.

**Table S4** Hydrogen bonding data of **1**, **2** and **3**.

| **1** | | | | |
|---|---|---|---|---|
| *D*-H···A | d(*D*-H) / Å | d(H···A) / Å | d(*D*···A) / Å | *D*-H···A / ° |
| C(2)-H(2)···O(6) #1 | 0.95 | 2.56 | 3.337(4) | 139 |
| C(8)-H(8)···O(4) #2 | 0.95 | 2.46 | 3.357(15) | 157 |
| C(12)-H(12)···O(5) #3 | 0.95 | 2.60 | 3.330(4) | 134 |
| C(12)-H(12)···O(7) #3 | 0.95 | 2.58 | 3.399(5) | 144 |
| C(15)-H(15)···O(7) #3 | 0.95 | 2.47 | 3.369(4) | 159 |
| C(17)-H(17)···N(13) #4 | 0.95 | 2.36 | 3.280(4) | 163 |
| C(24)-H(24)···O(7) #5 | 0.95 | 2.53 | 3.268(5) | 134 |
| C(27)-H(27)···O(2) #6 | 0.95 | 2.49 | 3.332(11) | 147 |
| C(27)-H(27)···O(3A) #6 | 0.95 | 2.41 | 3.353(15) | 171 |
| C(30)-H(30)···O(3A) #6 | 0.95 | 2.58 | 3.522(17) | 174 |
| C(35)-H(35)···O(2A) #3 | 0.95 | 2.51 | 3.423(11) | 160 |
| C(38)-H(38)···O(6) #7 | 0.95 | 2.57 | 3.178(4) | 122 |
| C(44)-H(44)···O(3) #3 | 0.95 | 2.42 | 3.163(15) | 135 |
| C(47)-H(47)···O(4) #2 | 0.95 | 2.39 | 3.325(16) | 167 |
| **2** | | | | |
| *D*-H···A | d(*D*-H) / Å | d(H···A) / Å | d(*D*···A) / Å | *D*-H···A / ° |
| C(25)-H(25)···N(1) #3 | 0.93 | 2.53 | 3.432(5) | 163 |
| C(26)-H(26)···O(2) #4 | 0.93 | 2.43 | 3.352(4) | 169 |
| C(29)-H(29)···O(4) #5 | 0.93 | 2.50 | 3.271(4) | 140 |
| C(35)-H(35)···O(3) #6 | 0.93 | 2.46 | 3.271(6) | 145 |
| **3** | | | | |
| *D*-H···A | d(*D*-H) / Å | d(H···A) / Å | d(*D*···A) / Å | *D*-H···A / ° |
| C(2)-H(2)···O(3) #1 | 0.95 | 2.39 | 3.234(4) | 147 |
| C(7)-H(7)···O(4) #2 | 0.95 | 2.38 | 3.188(2) | 143 |
| C(8)-H(8)···O(3) #1 | 0.95 | 2.58 | 3.401(3) | 145 |
| C(14)-H(14)···N(1) #3 | 0.95 | 2.56 | 3.478(3) | 163 |
| C(15)-H(15)···O(1) #4 | 0.95 | 2.41 | 3.340(3) | 166 |

Symmetry codes: #1 1+x,y,-1+z; #2 -x,1-y,2-z; #3 -x,1-y,1-z; #4 x,y,1+z; #5 1+x,y,z; #6 1-x,1-y,1-z; #7 x,y,z for **1**; #1 -1-x,-y,1-z; #2 -1-x,1-y,-z; #3 x,1+y,z; #4 -1-x,1-y,1-z; #5 1+x,y,z; #6 1+x,1+y,z for **2**; #1 1-x,2-y,1-z; #2 -1+x,y,z; #3 x,y,-1+z; #4 3-x,1-y,1-z for **3**.

**Table S5** $K_{sv}$ values for fluorescent detecting TNP.

| Sample | $K_{sv}$ / $M^{-1}$ | Ref. |
|---|---|---|
| **1** | $3.94 \times 10^4$ | This work |
| **2** | $4.78 \times 10^4$ | This work |
| **3** | $5.01 \times 10^4$ | This work |
| $[Zn_2(tipe)(tpe)]\cdot 3MeOH\cdot 13H_2O$ | $2.08 \times 10^4$ | [13] |
| $[Zn_4(\mu_3\text{-}OH)_2(BTC)_2\ (BBI_4PY)_2]\cdot 10H_2O$ | $2.94\times10^4$ | [14] |
| $Cd(NDC)(H_2O)$ | $2.385\times10^4$ | [15] |
| $[Zn_2(L)(DMF)_3]\cdot 2DMF\cdot 2H_2O$ ($H_4L$=terphenyl-3,3″,5,5″-tetracarboxylic acid) | $2.61 \times 10^4$ | [16] |

**Table S6** Standard deviation and limit of detection (LOD) calculation for TNP in DMA suspension.

| | **1** | **2** | **3** |
|---|---|---|---|
| 1 | 753.432676 | 963.690498 | 944.961405 |
| 2 | 753.733048 | 963.882307 | 944.687457 |
| 3 | 753.873114 | 963.901308 | 944.858592 |
| Standard deviation (σ) | 0.22503 | 0.11661 | 0.13839 |
| $K_{sv}$ (m) | $3.94 \times 10^4\ M^{-1}$ | $4.78 \times 10^4\ M^{-1}$ | $5.01 \times 10^4\ M^{-1}$ |
| LOD (3σ/m) | $1.71 \times 10^{-5}$ M | $7.32 \times 10^{-6}$ M | $8.29 \times 10^{-6}$ M |

**Table S7** Standard deviation and LOD calculation for TNP in $H_2O$ suspension.

| | **1** | **2** | **3** |
|---|---|---|---|
| 1 | 864.656857 | 820.841933 | 617.724435 |
| 2 | 865.023295 | 821.048489 | 617.528418 |
| 3 | 865.078827 | 821.187064 | 617.988924 |
| Standard deviation (σ) | 0.22928 | 0.173678 | 0.23110 |
| $K_{sv}$ (m) | $5.88 \times 10^3$ $M^{-1}$ | $6.90 \times 10^3$ $M^{-1}$ | $2.13 \times 10^4$ $M^{-1}$ |
| LOD (3σ/m) | $1.17 \times 10^{-4}$ M | $7.55 \times 10^{-5}$ M | $3.25\times 10^{-5}$ M |

**Table S8** Standard deviation and LOD calculation for 4-MB in DMA suspension of **2**.

| | **2** |
|---|---|
| 1 | 980.433837 |
| 2 | 980.887501 |
| 3 | 980.401471 |
| Standard deviation (σ) | 0.22188 |
| $K_{sv}$ (m) | $1.05 \times 10^5$ $M^{-1}$ |
| LOD (3σ/m) | $6.34 \times 10^{-6}$ M |

**Table S9** Standard deviation and LOD calculation for DBDPO in $H_2O$ suspension.

| | **1** | **2** | **3** |
|---|---|---|---|
| 1 | 693.443260 | 869.070951 | 734.395858 |
| 2 | 693.975506 | 869.535634 | 734.982327 |
| 3 | 693.544505 | 869.519121 | 734.460143 |
| Standard deviation (σ) | 0.22928 | 0.21527 | 0.26263 |
| $K_{sv}$ (m) | $1.76 \times 10^2$ $M^{-1}$ | $1.33 \times 10^2$ $M^{-1}$, | $2.62 \times 10^2$ $M^{-1}$ |
| LOD (3σ/m) | $3.91 \times 10^{-3}$ M | $4.86 \times 10^{-3}$ M | $3.01\times 10^{-3}$ M |

**Table S10** Lifetimes of **1**, **2** and **3** dispersed in DMA or water before and after the addition of TNP solution.

| Item | DMA | | | $H_2O$ | | |
|---|---|---|---|---|---|---|
| | **1** | **2** | **3** | **1** | **2** | **3** |
| Before quenching / ns | 0.65 | 0.74 | 0.46 | 0.91 | 0.78 | 0.50 |
| After quenching / ns | 0.64 | 0.71 | 0.44 | 0.64 | 0.76 | 0.49 |

**Table S11** Frontier molecular orbital energies for TNP and **1**, **2** and **3** at the generalized gradient approximation PerdewBurke-Ernzerhof (GGA-PBE) level of theory.

| Samples | VB / eV | CB / eV | Energy Gap / eV |
|---|---|---|---|
| **1** | -5.474 | -3.815 | 1.658 |
| **2** | -6.290 | -4.130 | 2.160 |
| **3** | -6.399 | -4.235 | 2.164 |
| TNP | -7.430 (HOMO) | -5.240 (LUMO) | 2.187 |

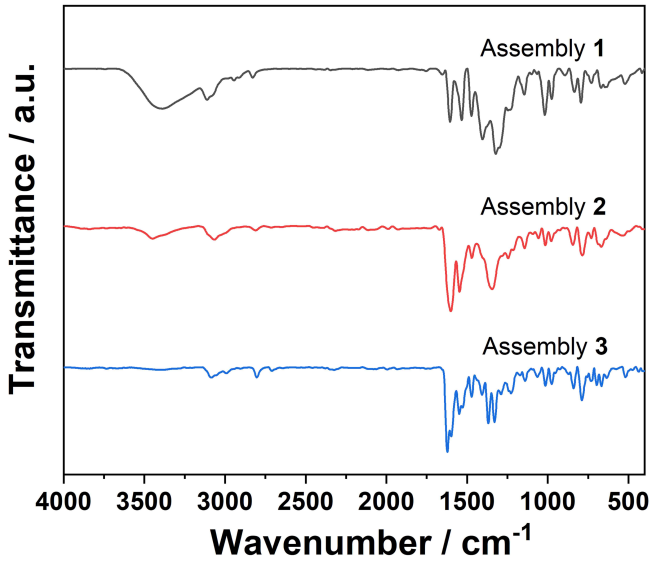


**Fig. S1** FTIR-ATR spectra of **1**, **2** and **3**.

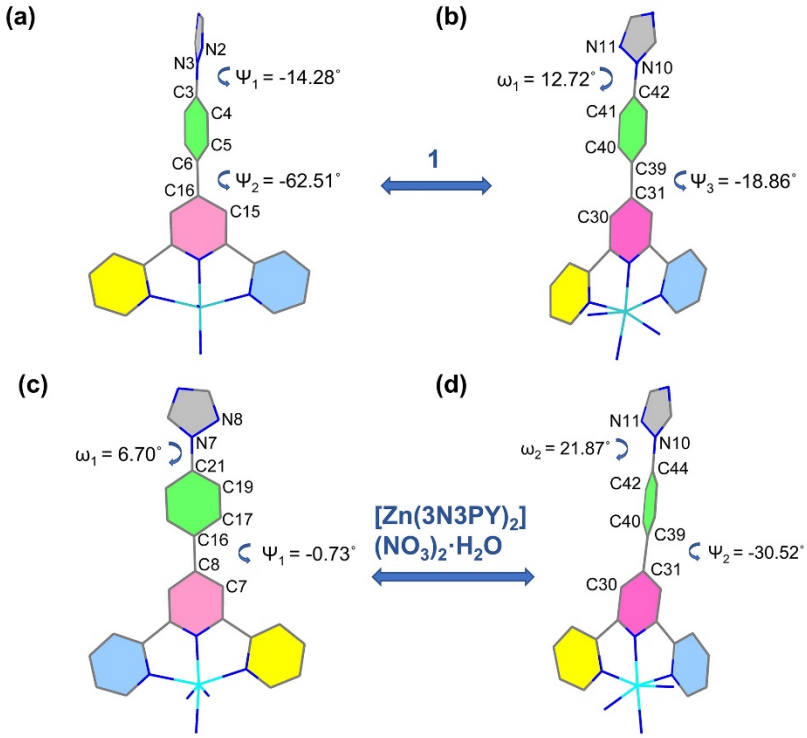


**Fig. S2** Selected torsion angles (°) for **1** viewing towards plane (h, k, l) = (4, 4, -1) (a), (4, -13, -1) (b) and reported $[Zn(3N3PY)_2](NO_3)_2 \cdot H_2O$ to (-1, -1, 3) (c) and (-8, 5, -1) (d).

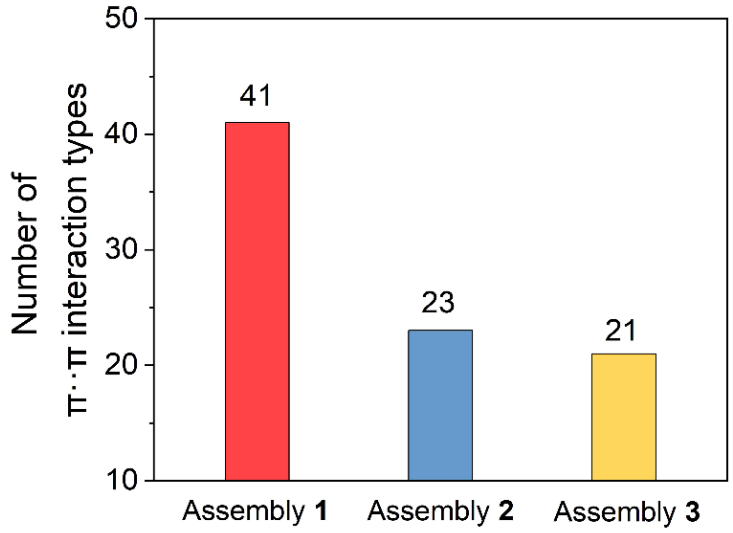


**Fig. S3** The number of π-π interaction types for **1**, **2** and **3**.

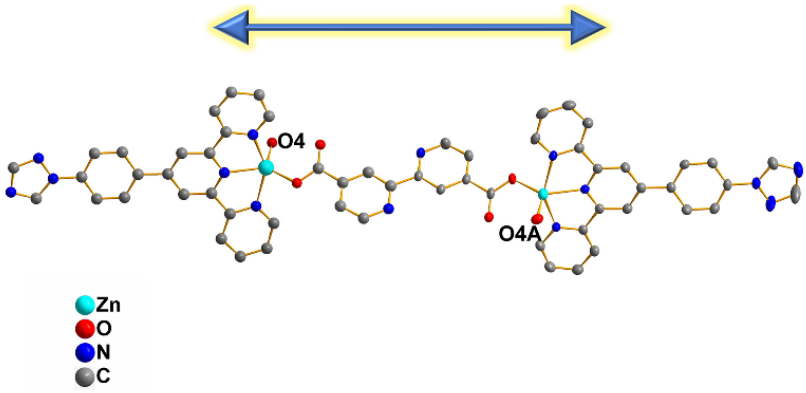


**Fig. S4** Double-arrow unit in **2**.

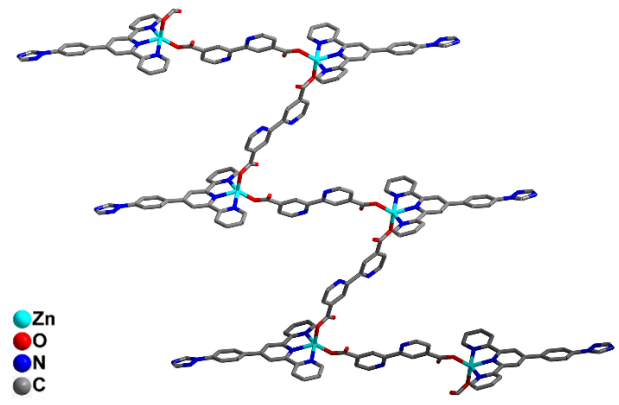


**Fig. S5** 1D chain structure of **2**.

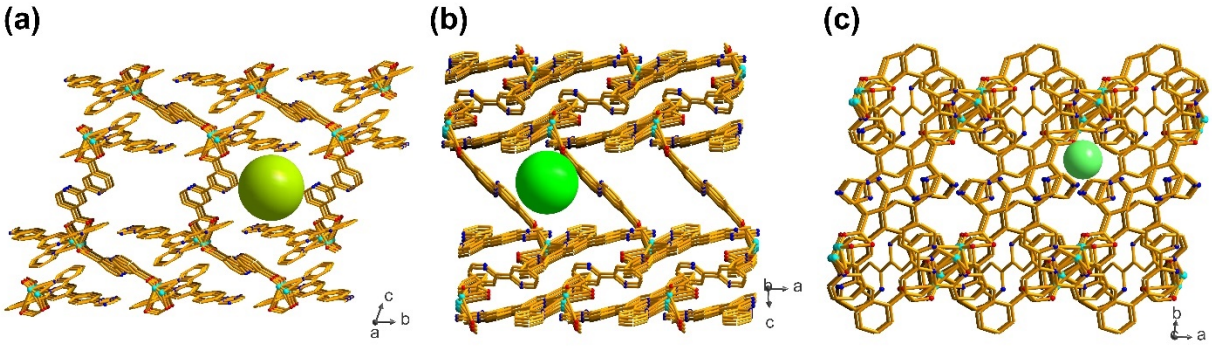


**Fig. S6** The micropores in **2** by the stacking of 1D chains.

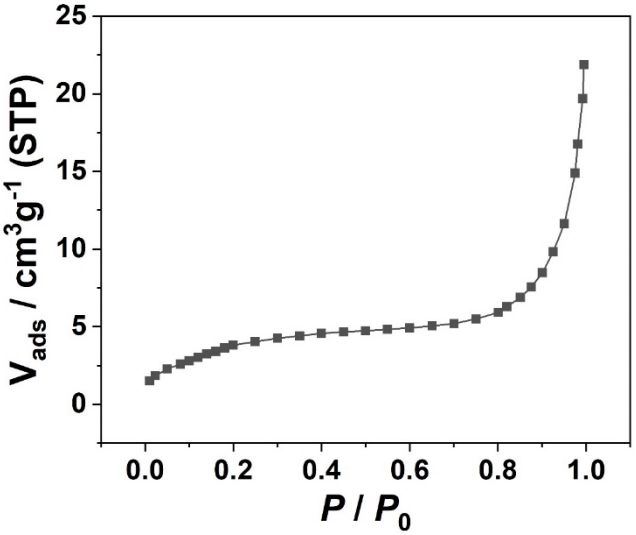


**Fig. S7** $N_2$ adsorption isotherm at 77 K of assembly **2**.

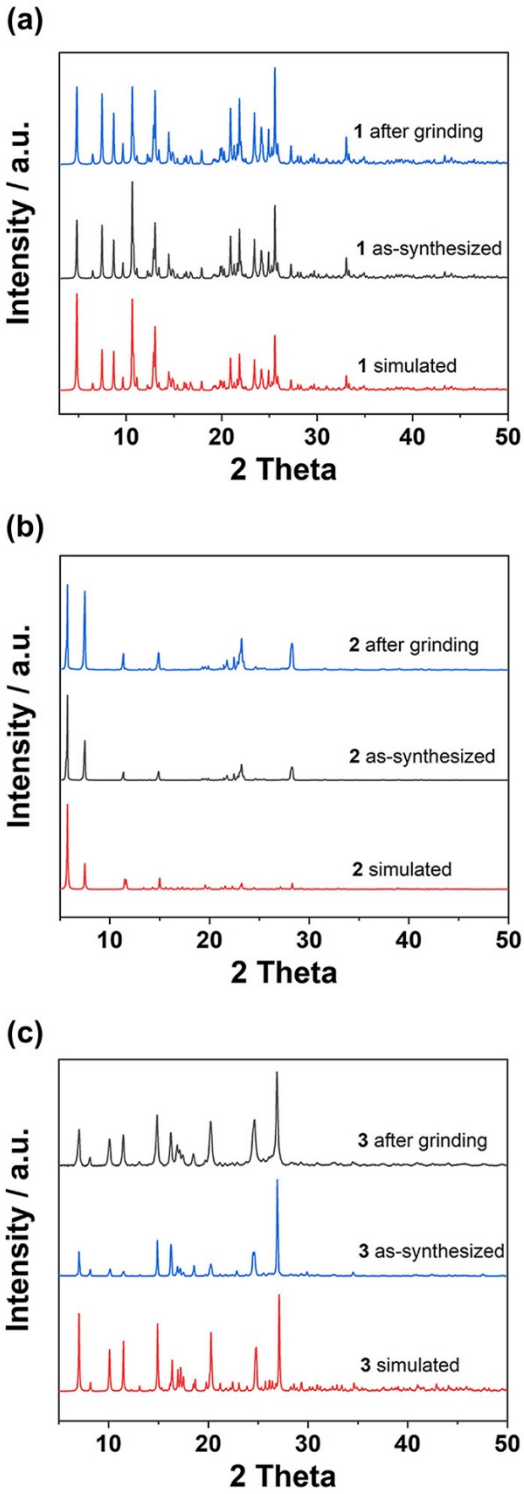


**Fig. S8** PXRD patterns of **1** (a), **2** (b) and **3** (c).

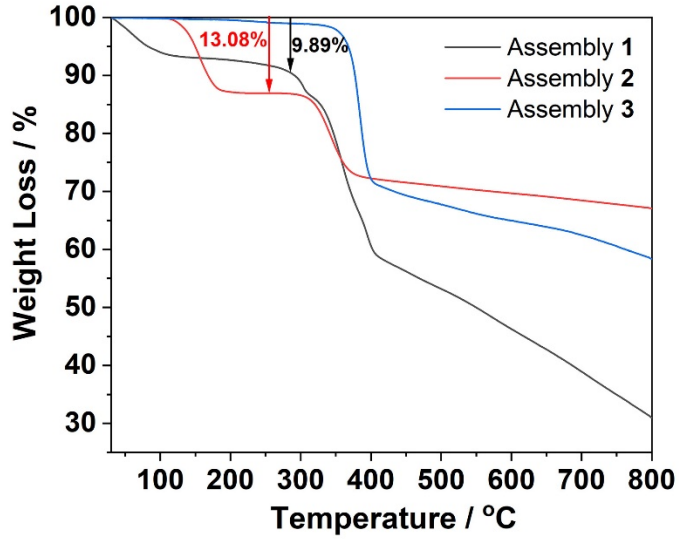


**Fig. S9** TG curves of **1**, **2** and **3**.

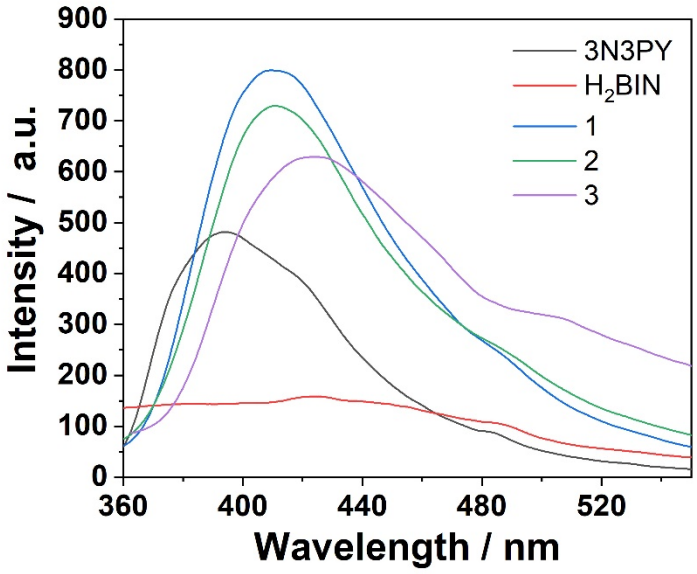


**Fig. S10** Photoluminescence spectra of 3N3PY, $H_2$BIN, **1**, **2** and **3** in solid state ($\lambda_{ex}$ = 330 nm).

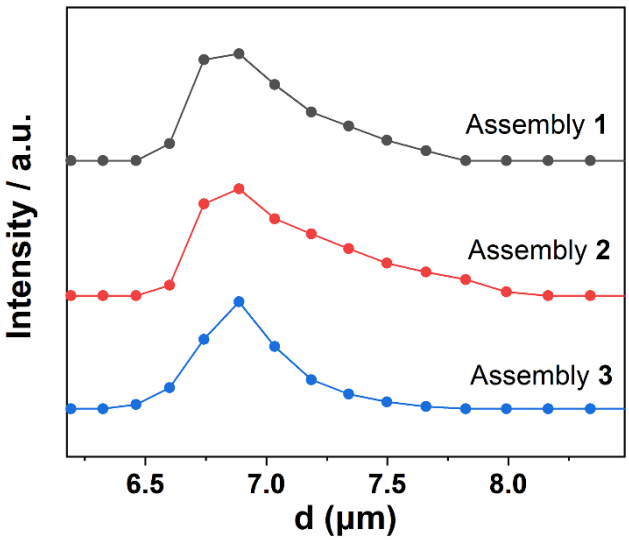


**Fig. S11** DLS results of **1**, **2** and **3** in aqueous suspension.

The quenching efficiency (Φ) was determined by the following equation:

$$\Phi = 1 - I / I_0$$

where $I_0$ and I are the emission intensities without and with the presence of TNP.

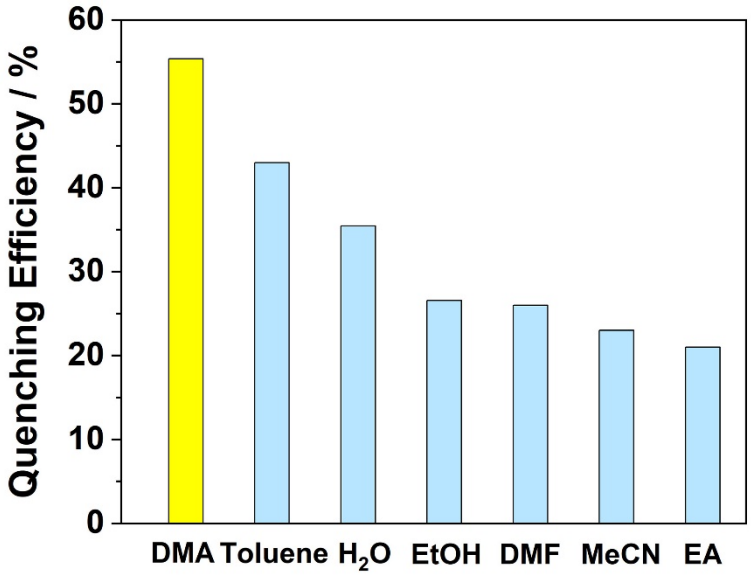


**Fig. S12** Quenching efficiency (1-I / $I_0$) of **1** by the corresponding TNP solution in different solvent.

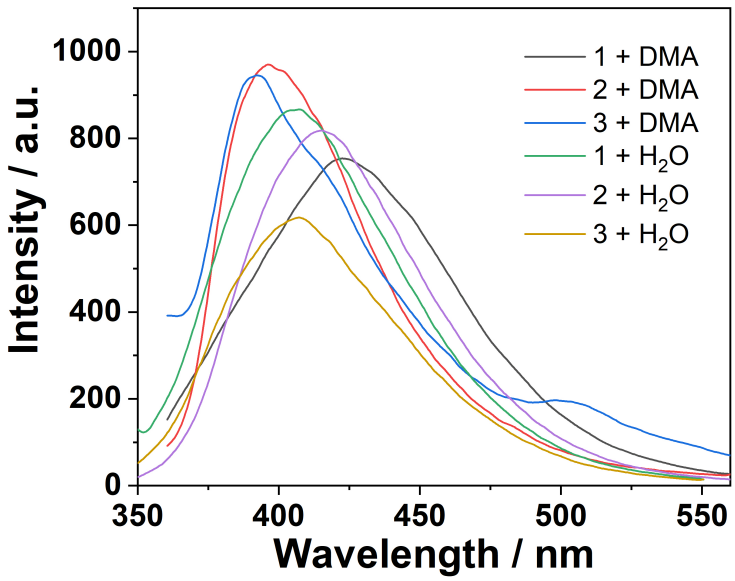


**Fig. S13** Fluorescence spectra of **1**, **2** and **3** suspended in DMA and $H_2O$.

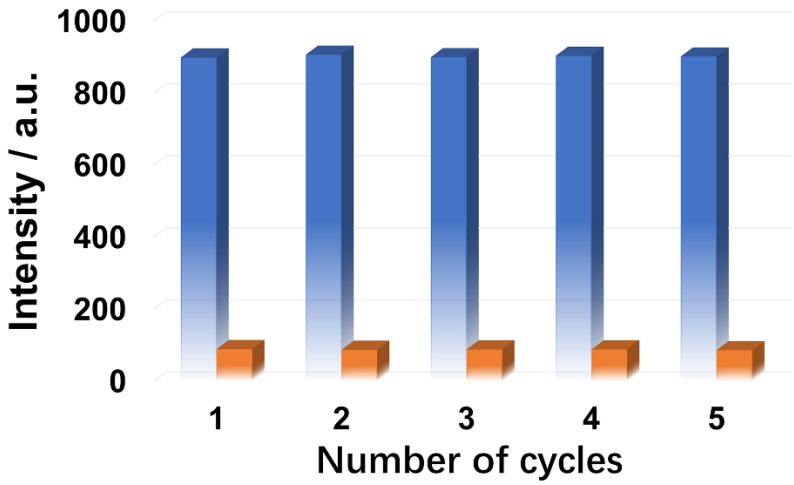


**Fig. S14** Fluorescence quenching and repeatability test for **3** with initial fluorescence intensity (blue) and intensity after quenching (orange).

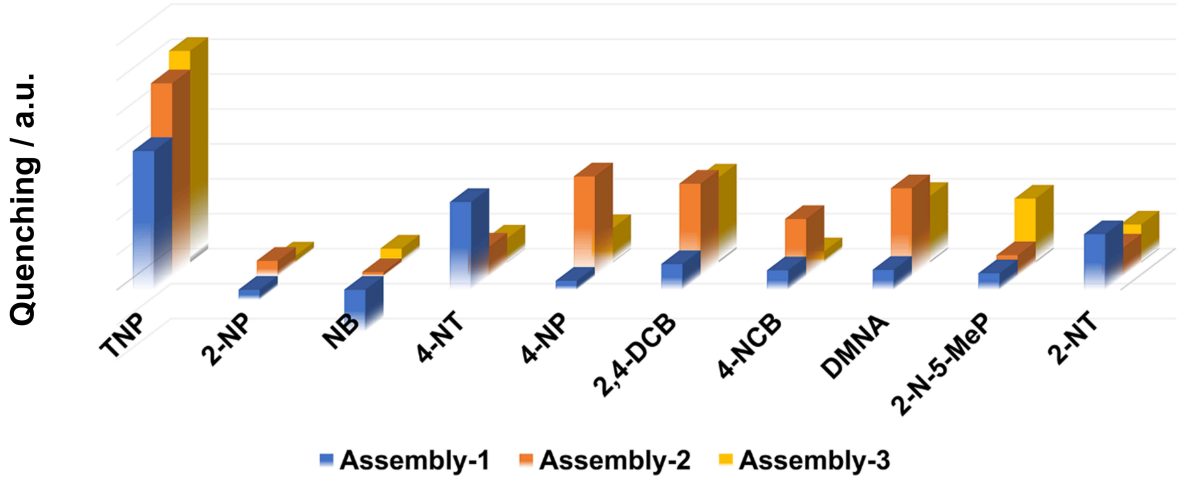


**Fig. S15** Fluorescence quenching of **1**, **2** and **3** upon addition of the same amount of NACs including TNP, 2-nitrophenol (2-NP), nitrobenzene (NB), 4-nitrotoluene (4-NT), 4-nitrophenol (4-NP), 2,4-dinitrochloroben (2,4-DCB), 4-nitrochlorobenzene (4-NCB), 4,5-dimethyl-2-nitroaniline (DMNA), 5-methyl-2-nitrophenol (2-N-5-MeP) and 2-nitrotoluene (2-NT).

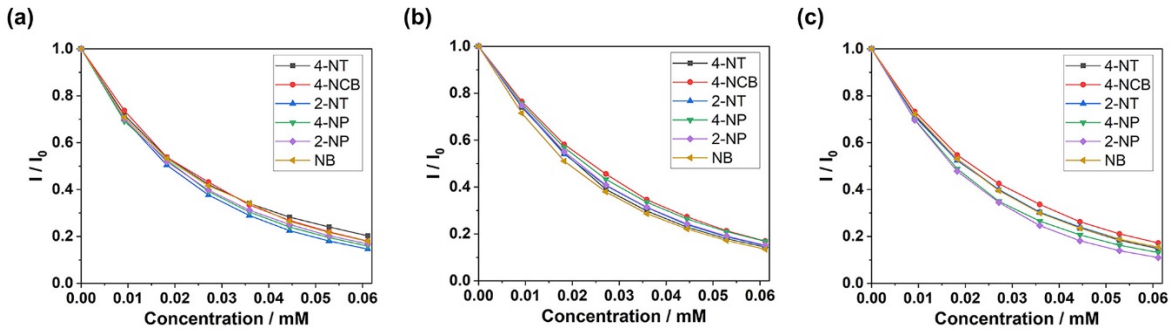


**Fig. S16** Selective detection of TNP on **1** (a), **2** (b) and **3** (c) in the presence of other NACs in DMA suspensions.

The derivation process of the modified Stern-Volmer (S-V) equation is presented below.

Firstly, according to the previous report, the S-V equation was allowed to be written as a function of $\Phi$ as eqn. S1[11]

$$\Phi = 1 - I / I_0 = 1 - 1 / (1 + K_{sv}\, Q_t) \quad \text{(S1)}$$

where $\Phi$ is quenching efficiency, $K_{sv}$ is the S-V constant and $Q_t$ is the uptake amount of the analyte vapour at time *t* by the sensor.

Accordingly, $Q_t$ is reasonable to be replaced by eqn. S2 since the diffusion or adsorption-controlled process in a solid-state gas sensor can be described by a pseudo-second order kinetics.[11,12]

$$Q_t = Q_\infty\, k_2\, t / (1 + k_2\, t) \quad \text{(S2)}$$

where $Q_\infty$ is the uptake amount of analyte vapour at equilibrium and $k_2 = k\, Q_\infty$ with $k$ to be the kinetic constant. The final modified S-V equation can be written as eqn. S3:

$$\Phi = K\, k_2\, t / (1 + k_2\, t + K\, k_2\, t) \quad \text{(S3)}$$

where $K = Q_\infty \times K_{sv}$.

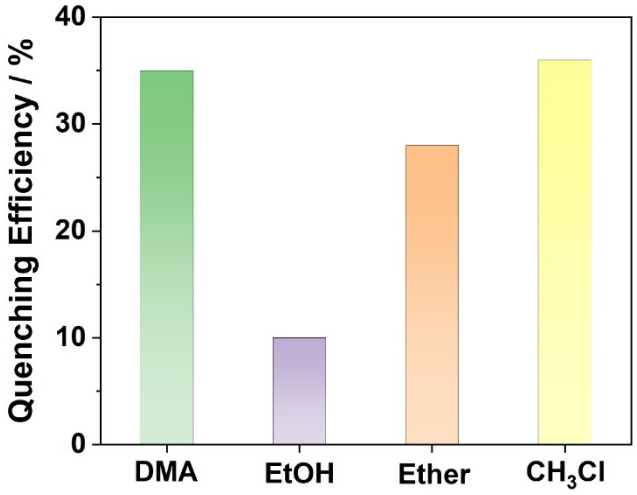


**Fig. S17** Quenching efficiency ($1-I/I_0$) of **2** by adding 2 μL 4-MB respectively in DMA, EtOH, ether, and chloroform ($CH_3Cl$) suspensions (0.5 mg/mL).

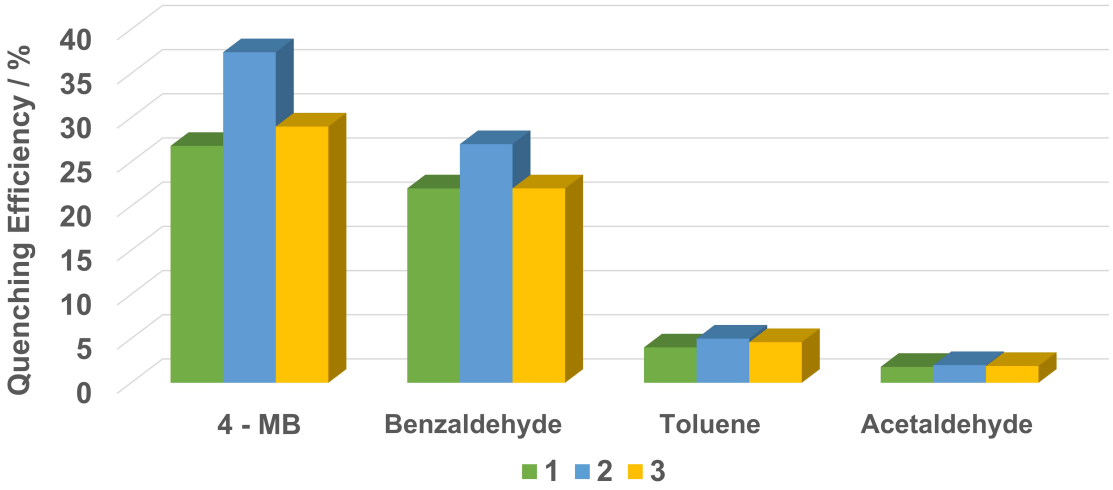


**Fig. S18** Quenching efficiency ($1-I/I_0$) of **1, 2, 3** (0.5 mg/mL) for organic molecules.

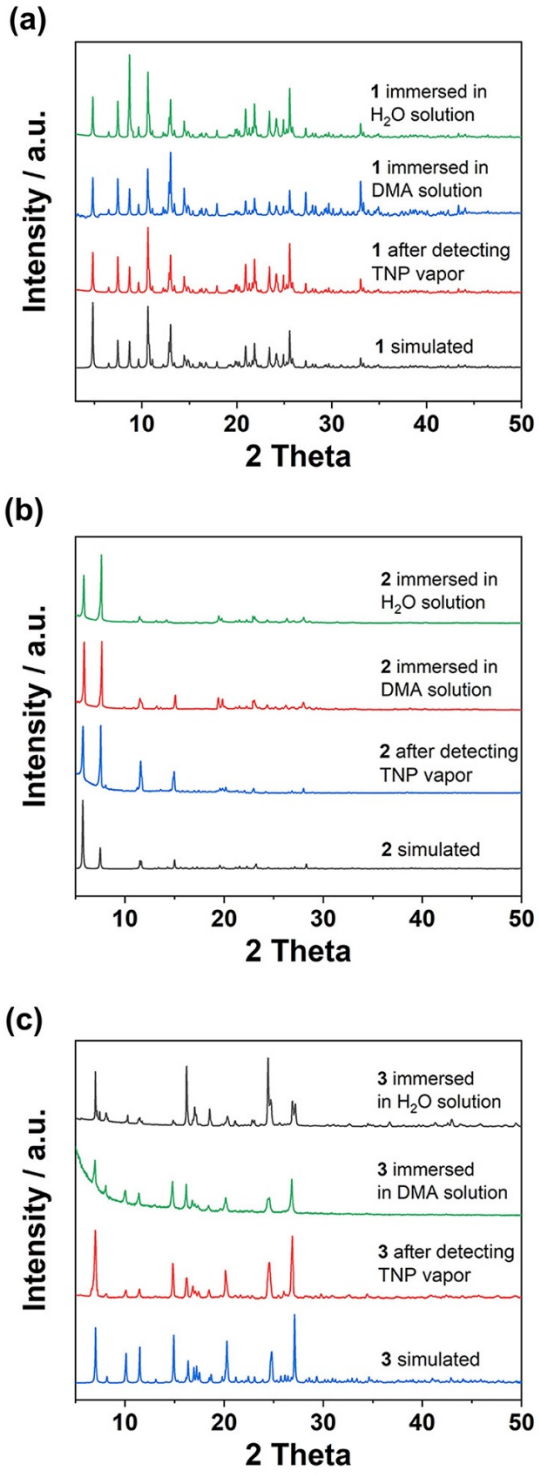


**Fig. S19** PXRD patterns of **1** (a), **2** (b) and **3** (c) before and after immersing in $H_2O$ or DMA solution of TNP and detecting TNP vapour.

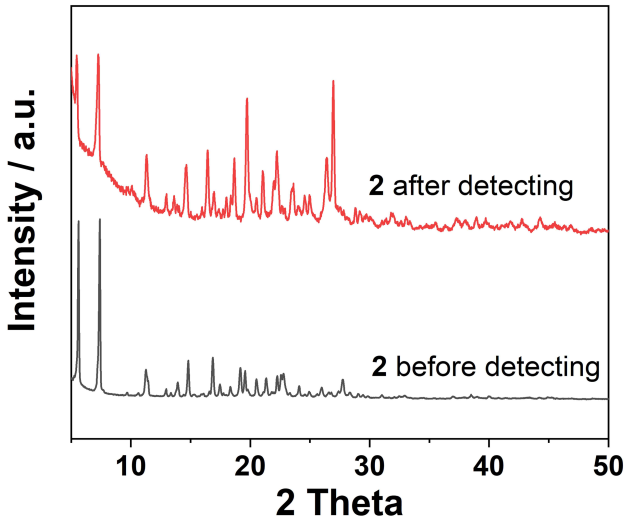


**Fig. S20** PXRD patterns of **2** before and after detecting 4-MB.

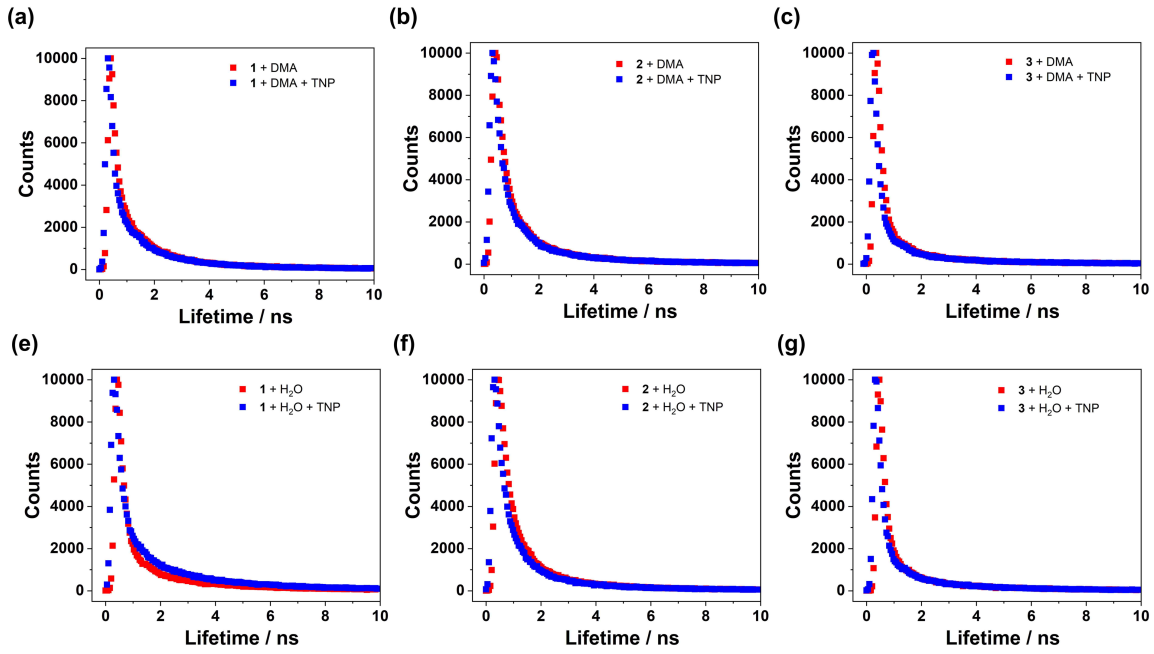


**Fig. S21** Lifetimes of **1** (a), **2** (b) and **3** (c) dispersed in DMA before and after the addition of TNP solution. The solvent was changed to water for **1** (e), **2** (f) and **3** (g).

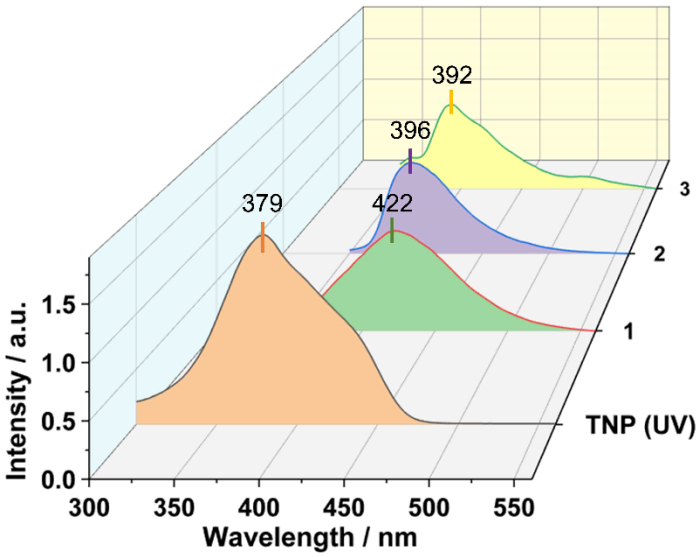


**Fig. S22** Absorption spectra of TNP solution and normalized emission spectra of **1**, **2** and **3** stock suspension in DMA.

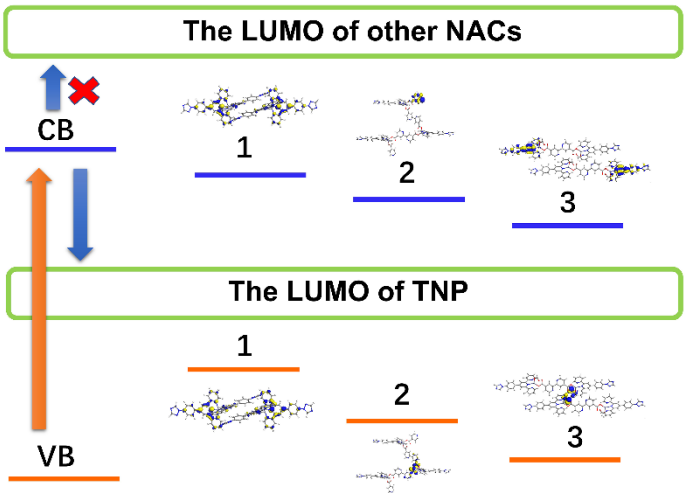


**Fig. S23** Proposed PET process during the fluorescent quenching of **1**, **2** and **3** for TNP.

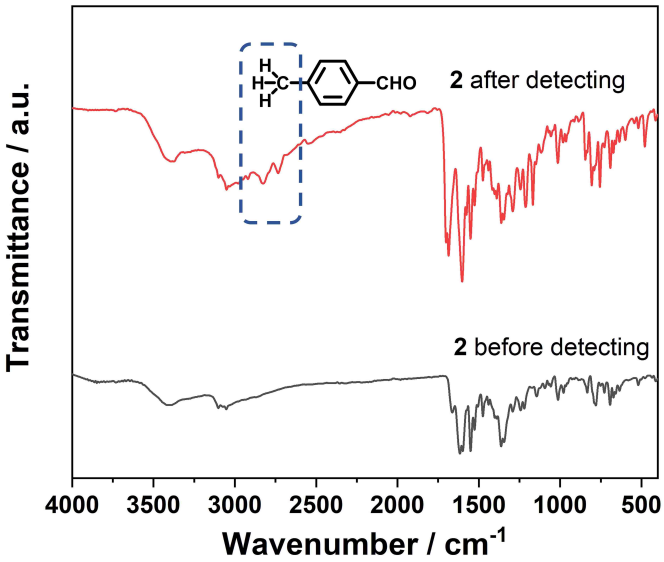


**Fig. S24** FTIR-ATR spectra of **2** before and after detecting 4-MB.

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