

Electronic Supplementary Information

ESI

New Cyanido-Bridged Complexes of Zn(II) and/or Ag(I) with TPymT and Tptz Ligands: Synthesis, Structural and Fluorescent Properties

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Table S1. Selected bond lengths [Å] and angles [°] for **1** and **2**

| 1 | | 2 | | 1 | | 2 | |
|------------------------|------------|------------|------------|-------------|-----------|---------------|-----------|
| Ag1 - Ag2 ¹ | 3.0244(14) | Ag1 - Ag3b | 3.3740(11) | C21-Ag1-C20 | 171.1(4) | N7-Ag1-N8 | 65.61(19) |
| Ag1 - C20 | 2.051(12) | Ag1 - N7 | 2.466(6) | C18-Ag2-C19 | 176.6(5) | Ag1-N11a-C17a | 98.0(3) |
| Ag1 - C21 | 2.040(11) | Ag1 - N8 | 2.494(6) | O31-Zn1-N1 | 89.1(3) | Ag3-N11-C17 | 178.0(4) |
| Ag2 - Ag2 ² | 3.0719(16) | Ag1 - N4 | 2.6985(64) | O31-Zn1-N2 | 87.0(3) | Ag3-N18-C12 | 174.65 |
| Ag2 - C18 | 2.046(12) | Ag1 - N23b | 2.152(9) | O31-Zn1-N7 | 175.4(3) | Ag3-N10-C16 | 153.71 |
| Ag2 - C19 | 2.047(12) | Ag2 - N3 | 2.427(6) | N3-Zn1-O31 | 89.3(3) | Ag6-N25-C36 | 165.48 |
| Zn1 - O31 | 2.146(7) | Ag2 - N5 | 2.391(5) | N3-Zn1-N7 | 90.2(3) | Ag6-C35-N23 | 169.96 |
| Zn1 - N1 | 2.273(7) | Ag2 - C16 | 2.093(7) | C18-N7-Zn1 | 155.4(9) | Ag6-N22-C34 | 150.25 |
| Zn1 - N2 | 2.214(7) | Ag2 - N1 | 2.621(7) | C20-N9-Zn1 | 171.6(9) | Ag5-C34-N22 | 175.78 |
| Zn1 - N3 | 2.084(7) | Ag3 - N11 | 2.43(4) | N7-Zn1-N1 | 95.1(3) | Ag4-N12-C18 | 167.56 |
| Zn1 - N7 | 2.161(10) | Ag3 - N10 | 2.281(8) | N7-Zn1-N2 | 88.5(3) | Ag2-C16-N10 | 175.12 |
| Zn1 - N9 | 2.011(9) | Ag3 - C18 | 2.102(7) | N9-Zn1-O31 | 89.4(3) | Ag1-N23a-C35a | 172.13 |
| | | Ag4 - Ag6c | 3.0924(10) | N9-Zn1-N1 | 98.6(3) | Ag1-N11b-C17b | 97.77 |
| | | Ag4 - N13 | 2.572(6) | N9-Zn1-N2 | 113.4(3) | C35-Ag6-N25 | 135.39 |
| | | Ag4 - N15 | 2.586(6) | N9-Zn1-N3 | 171.8(3) | N10-Ag3-N11 | 95.40 |
| | | Ag4 - N17 | 2.440(5) | N9-Zn1-N7 | 91.7(3) | C35-Ag6-N22 | 122.94 |
| | | Ag4 - C36c | 2.666(9) | N7-C18-Ag2 | 173.8(10) | C18-Ag3-N11 | 129.94 |
| | | Ag4 - N12 | 2.183(7) | N8-C19-Ag2 | 177.2(13) | | |
| | | Ag5 - N16 | 2.394(6) | N9-C20-Ag1 | 175.8(10) | | |
| | | Ag5 - N18 | 2.417(6) | N10-C21-Ag1 | 176.2(11) | | |
| | | Ag5 - N20 | 2.666(7) | | | | |
| | | Ag5 - C34 | 2.104(7) | | | | |
| | | Ag6 - N22 | 2.343(7) | | | | |
| | | Ag6 - N25 | 2.222(8) | | | | |
| | | Ag6 - C35 | 2.100(9) | | | | |

¹*x, y, 1+z*; ²*1-x, 1-y, z*^a*1+x, 3/2-y, 1/2+z*; ^b*2-x, -y, 1-z*; ^c*1-x, 2-y, 1-z*

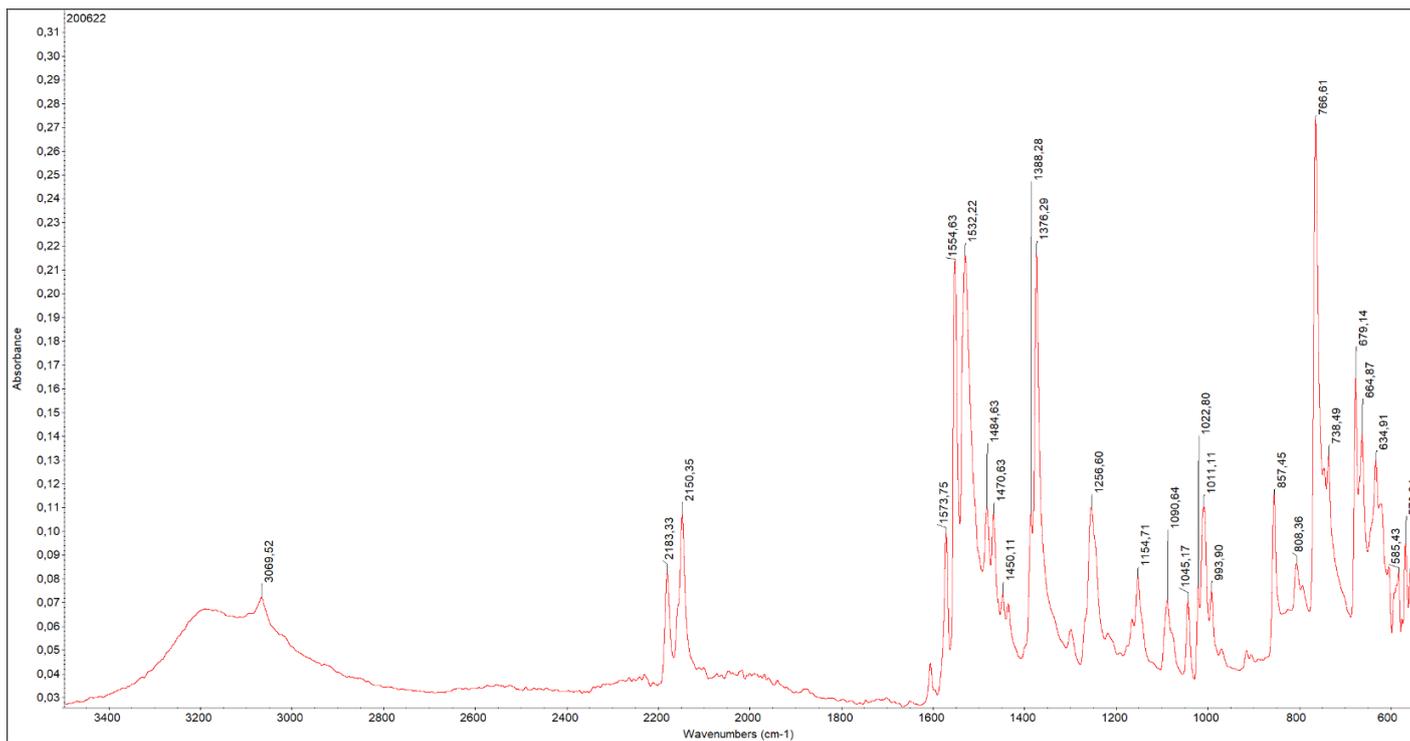


Figure S1. FTIR spectrum of 1

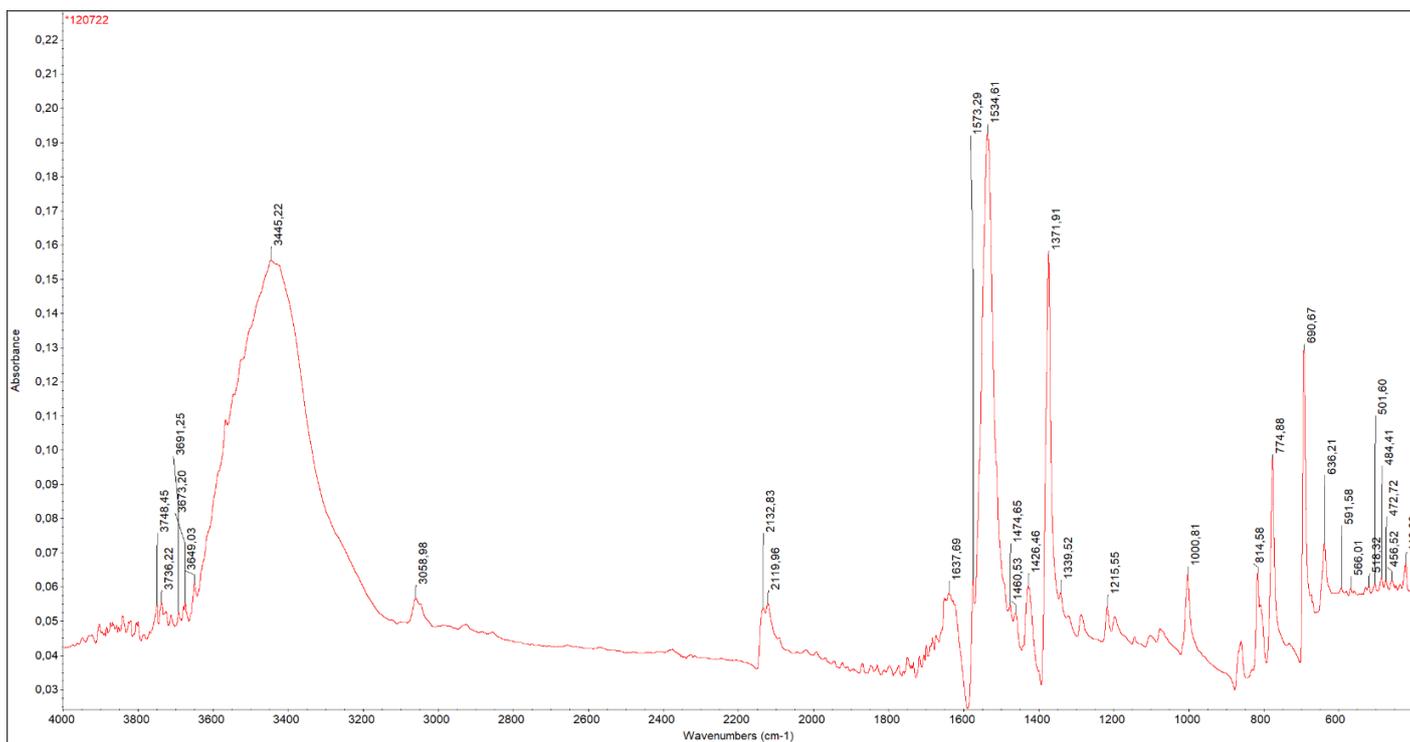


Figure S2. FTIR spectrum of 2

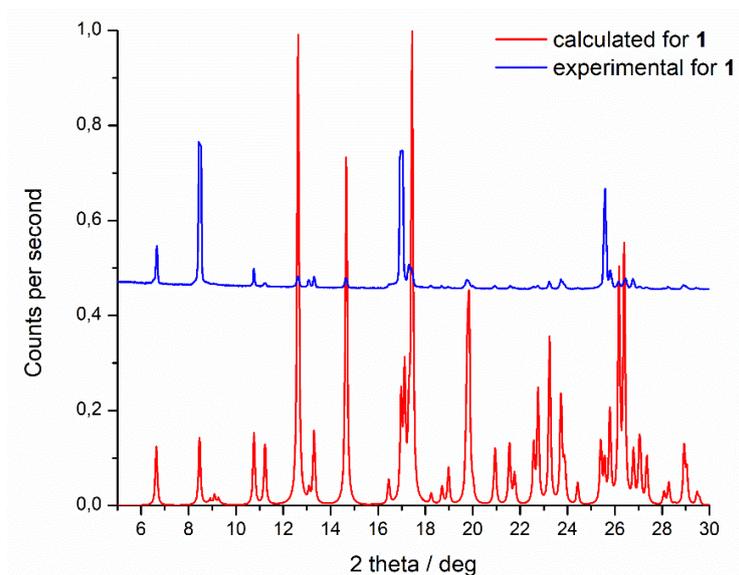


Figure S3. XRD on powder for **1**.

Table S2. Summary of the SHAPE analysis for the $[\text{AgC}_2]$ and $[\text{ZnN}_5\text{O}]$ fragments in **1***

| CN = 2 ^a | Ag1 | Ag2 |
|---------------------|--------------|--------------|
| L-2 | 0.202 | 0.030 |
| vT-2 | 11.292 | 13.104 |
| vOC-2 | 21.218 | 23.526 |
| CN = 6 ^b | Zn1 | |
| HP-6 | 33.272 | |
| PPY-6 | 23.889 | |
| OC-6 | 2.203 | |
| TPR-6 | 11.171 | |
| JPPY-6 | 27.541 | |

*The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values being given in bold.

^a L-2, D_{infh} , linear; vT-2, C_{2v} , Divacant tetrahedron; vOC-2, C_{2v} , Tetravacant octahedron; ^b HP-6, D_{6h} , hexagon; PPY-6, C_{5v} , Pentagonal pyramid; OC-6, O_h , octahedron; TPR-6, D_{3h} , Trigonal prism; JPPY-6, C_{5v} , Johnson pentagonal pyramid J2.

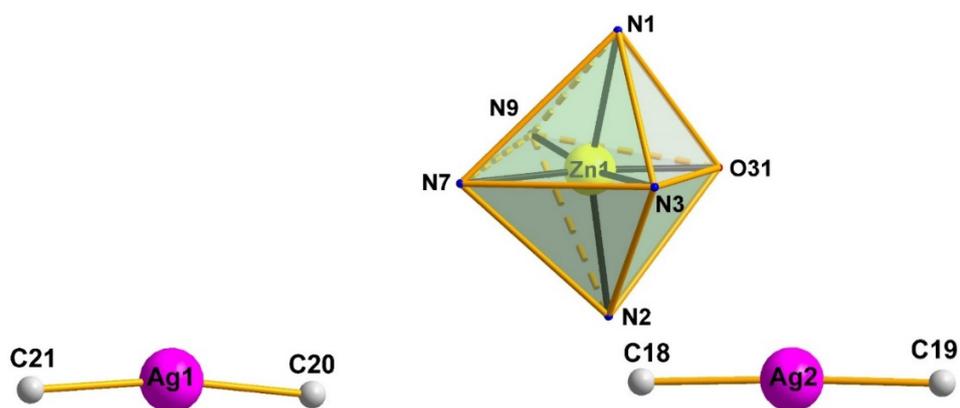


Figure S4. Distorted octahedron for Zn1 atom and linear surrounding geometries for Ag1 and Ag2 atoms in **1**.

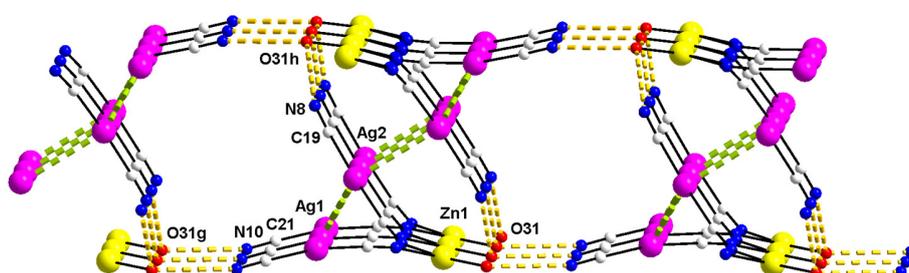


Figure S5. A fragment showing hydrogen bond established in **1**; $g = x, \frac{1}{2}+y, \frac{1}{2}+z$; $h = 1-x, 1-y, -1+z$.

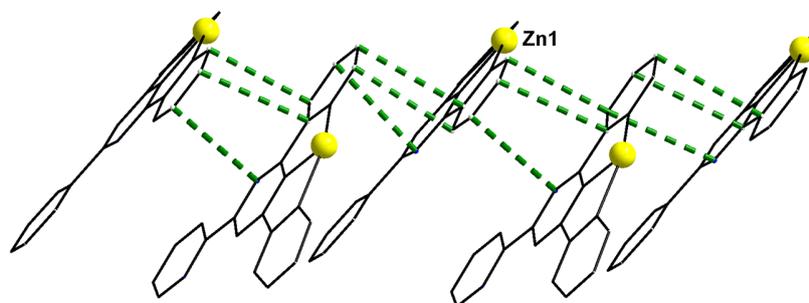


Figure S6. A fragment showing π - π stacking between the tptz aromatic rings in **1**.

Table S3. Hydrogen Bonds in **1**.

| D-H...A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|-------------------------------|----------|----------|-----------|---------|
| O31 ^g -H31B...N10* | 0.87 | 1.92 | 2.786(11) | 173 |
| O31 ^h -H31A...O8* | 0.87 | 1.91 | 2.751(15) | 161 |

* symmetry codes: g = x, 1/2+y, 1/2+z; h = 1-x, 1-y, -1+z.

Table S4. Summary of the SHAPE analysis for the [Ag(1,4)N₅], [Ag(2,5)CN₂], and [Ag(3,6)CN₃] fragments in **2***

| CN = 5 ^a | Ag1 | Ag4 |
|---------------------|--------------|--------------|
| PP-5 | 30.788 | 24.804 |
| vOC-5 | 6.558 | 6.759 |
| TBPY-5 | 7.542 | 7.648 |
| SPY-5 | 3.740 | 4.991 |
| JTBPY-5 | 10.512 | 11.439 |
| CN = 4 ^b | Ag2 | Ag5 |
| SP-4 | 5.143 | 5.583 |
| T-4 | 33.986 | 33.512 |
| SS-4 | 21.221 | 21.338 |
| vTBPY-4 | 28.674 | 28.391 |
| CN = 3 ^c | Ag3 | Ag6 |
| TP-3 | 1.671 | 1.022 |
| vT-3 | 3.732 | 3.316 |
| fvOC-3 | 10.844 | 10.679 |
| mvOC-3 | 7.252 | 6.279 |

*The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values being given in bold. ^aPP-5, *D*_{5h}, pentagon; vOC-5, *C*_{4v}, vacant octahedron; TBPY-5, *D*_{3h}, trigonal bipyramid; SPY-5, *C*_{4v}, spherical square pyramid; JTBPY-5, *D*_{3h}, Johnson trigonal bipyramid J12.

^b SP-4, Square, *D*_{4h}; T-4, Tetrahedron, *T*_d; SS-4, Seesaw, *C*_{2v}; vTBPY-4, Vacant trigonal bipyramid, *C*_{3v}.

^c TP-3, *D*_{3h}, Trigonal; vT-3, *C*_{3v}, Vacant tetrahedron; fvOC-3, *C*_{3v}, *fac*-Trivacant octahedron; mvOC-3, *C*_{2v}, *mer*-Trivacant octahedron.

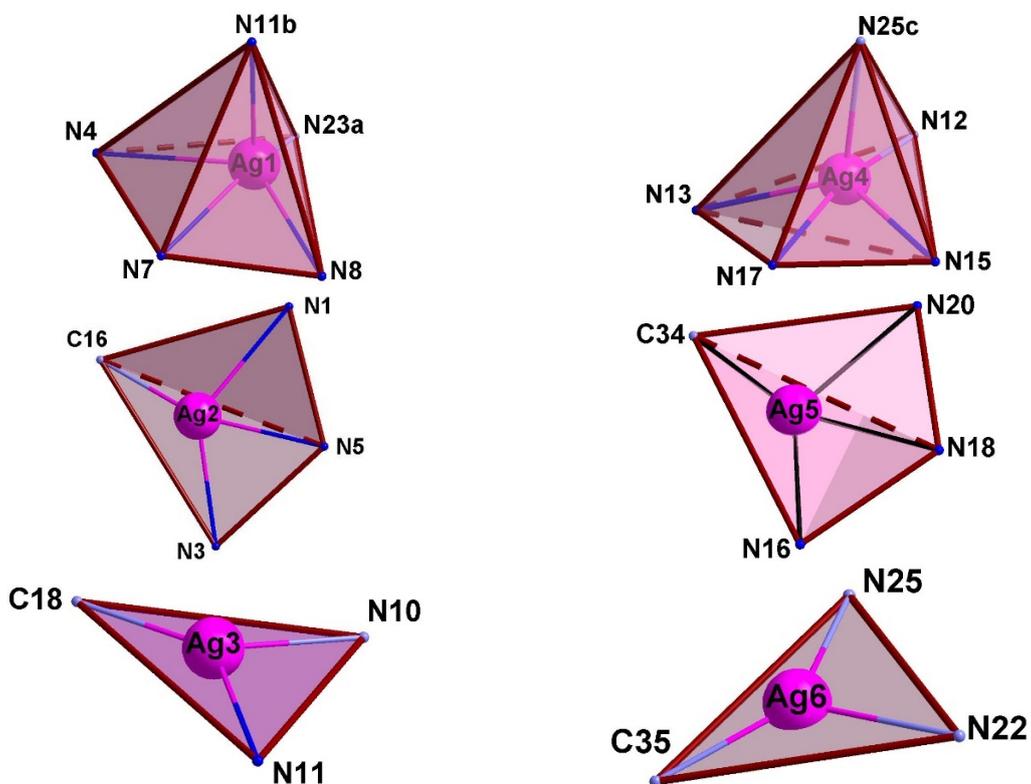


Figure S7. Distorted square pyramidal (for Ag1 and Ag4 atoms), square planar (for Ag2 and Ag5 atoms) and trigonal (for Ag3 and Ag6 atoms) surrounding geometries in **2**. Symmetry codes: $a = -1+x, 3/2-y, -1/2+z$; $b = 1-x, 3/2+y, 1/2-z$; $d = 1-x, 2-y, 1-z$

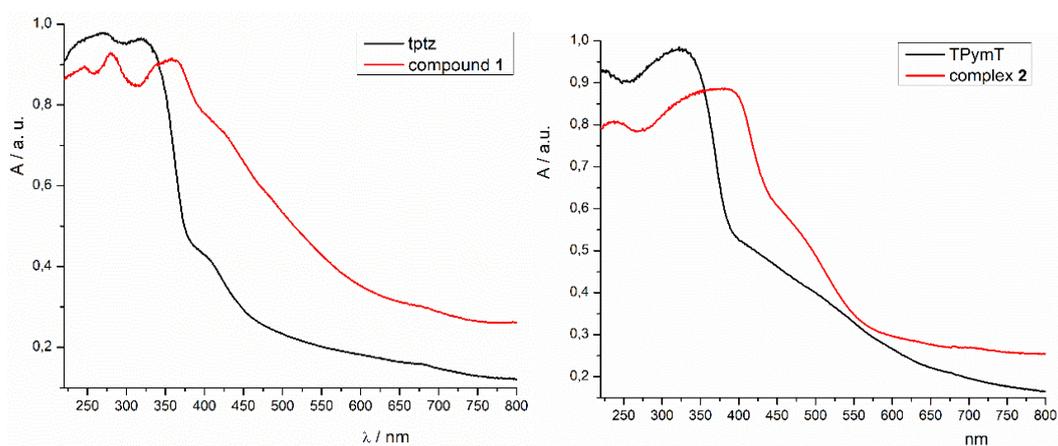


Figure S8. UV-Vis spectra of **1** (red line) and tptz (black line) - left; of **2** (red line) and TPymT (black line) – right.

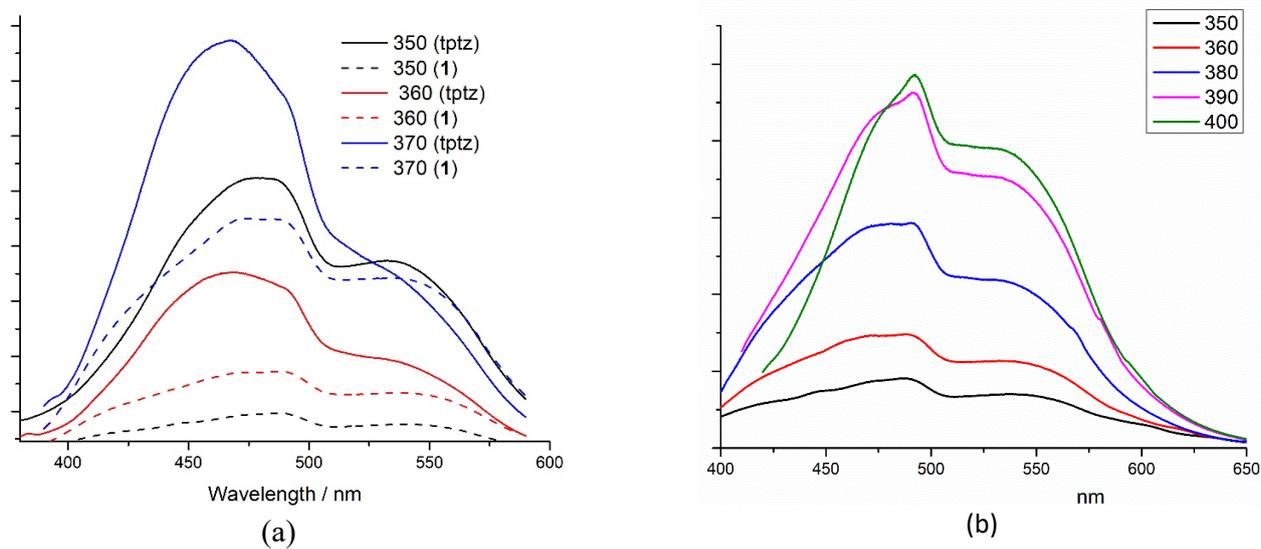


Figure S9. Emission spectra for: (a) **1** and tptz at $\lambda_{\text{exc}} = 350, 360$ and 370 nm; (b) **1** at $\lambda_{\text{exc}} = 350, 360, 380, 390$ and 400 nm.

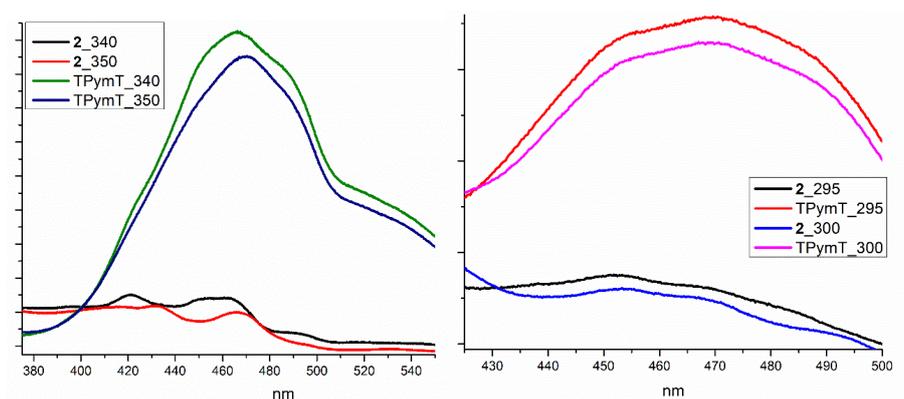


Figure S10. Emission spectra for **2** and TPymT excited at $\lambda = 340, 350$ nm (left) and at $295, 300$ nm (right).