# pH-Regulated Structural Evolution Enables Excitation-Dependent Tunable and Quasi-White-Light Emission in Tetrazole-Based $d^{10}$ Coordination Polymers

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**Table S1.** XRD Crystallographic Data for **1-3**

| Compound | **1** | **2** | **3** |
|---|---|---|---|
| CCDC | 1975825 | 1504873 | 1504881 |
| Formula | $C_{21}H_{14}CdN_6O_5$ | $C_{28}H_{22}CdN_{10}O_{10}$ | $C_{30}H_{20}N_{10}O_9Zn$ |
| Formula mass | 542.78 | 770.96 | 729.93 |
| Crystal system | Monoclinic | Triclinic | Triclinic |
| Space group | *C*2/c | *P*-1 | *P*-1 |
| *a*/Å | 31.1727(10) | 6.536(3) | 10.142(2) |
| *b*/Å | 6.8735(3) | 8.817(4) | 11.581(3) |
| *c*/Å | 19.5674(7) | 13.687(7) | 13.244(3) |
| *α*/° | 104.442(3) | 93.640(6) | 84.565(15) |
| *β*/° | 98.575(4) | 97.775(4) | 76.115(11) |
| *γ*/° | 104.442(3) | 98.916(8) | 77.104(15) |
| *V*/Å$^3$ | 4060.14(27) | 769.18(63) | 1470.63(59) |
| *Z* | 8 | 1 | 2 |
| $\rho_{calc}$ g/cm$^3$ | 1.776 | 1.664 | 1.648 |
| $\mu$/mm$^{-1}$ | 1.125 | 0.785 | 0.912 |
| *F*(000) | 2160 | 388 | 1789 |
| Reflections collected | 17746 | 6856 | 13278 |
| $wR_2$[b] *(all data)* | 0.053 | 0.070 | 0.179 |
| $R_1$ [a] *[I > 2s(I)]* | 0.020 | 0.028 | 0.034 |
| $R_{int}$ | 0.0228 | 0.0286 | 0.0737 |

[a]$R_1 = ||F_o| - |F_c||/|F_o|$. [b]$wR_2 = [w(F_o^2 - F_c^2)^2]/[w(F_o^2)^2]^{1/2}$.

**Table S2.** Selected lengths (Å) and angles (º) for the as-synthesized crystals of **1**.

| | | | |
|---|---|---|---|
| Cd1–O13 | 2.3656(11) | Cd1–N12 | 2.4168(13) |
| Cd1–N13#1 | 2.3683(12) | Cd1–O1W | 2.4295(13) |
| Cd1–N16#2 | 2.4006(13) | Cd1–O14 | 2.5605(11) |
| Cd1–N11 | 2.4023(12) | N12–Cd1–O1W | 84.03(5) |
| | | | |
| O13–Cd1–N13#1 | 104.48(4) | O13–Cd1–N16#2 | 84.30(4) |
| N13#1–Cd1–N16#2 | 163.01(4) | O13–Cd1–N11 | 78.69(4) |
| N13#1–Cd1–N11 | 93.48(4) | N16#2–Cd1–N11 | 102.59(4) |
| O13–Cd1–N12 | 146.86(4) | N13#1–Cd1–N12 | 86.60(5) |
| O13–Cd1–O14 | 52.60(3) | N16#2–Cd1–N12 | 93.84(4) |
| N13#1–Cd1–O14 | 92.41(5) | N11–Cd1–N12 | 69.41(5) |
| N16#2–Cd1–O14 | 81.33(4) | O13–Cd1–O1W | 127.93(4) |
| N11–Cd1–O14 | 130.79(4) | N13#1–Cd1–O1W | 82.15(4) |
| N12–Cd1–O14 | 159.77(4) | N16#2–Cd1–O1W | 81.02(4) |
| N11–Cd1–O1W | 153.32(5) | O1W–Cd1–O14 | 75.83(4) |

**Symmetry codes for 1:** #1 $-x + 1/2, -y + 3/2, -z + 1$ ； #2 $-x + 1/2, -y + 1/2, -z + 1$.

**Table S3.** Selected lengths (Å) and angles (º) for the as-synthesized crystals of **2**.

| | | | |
|---|---|---|---|
| Cd1–N22#1 | 2.3024(19) | Cd1–O1W | 2.3238(17) |
| Cd1–N22 | 2.3025(19) | Cd1–N11 | 2.3994(19) |
| Cd1–O1W#1 | 2.3238(18) | Cd1–N11#1 | 2.3994(19) |
| | | | |
| N22#1–Cd1–N11#1 | 93.40 (7) | N22#1–Cd1–N11 | 86.60 (7) |
| N22–Cd1–N11#1 | 86.60 (7) | N22–Cd1–N11 | 93.40 (7) |
| O1W#1–Cd1–N11#1 | 89.72 (7) | O1W#1–Cd1–N11 | 90.28 (7) |
| O1W–Cd1–N11#1 | 90.28 (7) | O1W—Cd1—N11 | 89.72 (7) |
| N11–Cd1–N11#1 | 180.0 | N22#1–Cd1–N22 | 180.0 |
| N22#1–Cd1–O1W | 90.59 (7) | N22#1–Cd1–O1W#1 | 89.41 (7) |
| N22–Cd1–O1W | 89.41 (7) | N22–Cd1–O1W#1 | 90.59 (7) |
| O1W#1–Cd1–O1W | 180.00 (8) | | |

**Symmetry codes for 2:** #1 $-x, -y + 1, -z + 1$; #2 $-x + 1, -y, -z + 1$.

**Table S4.** Selected lengths (Å) and angles (º) for the as-synthesized crystals of **3**.

| | | | |
|---|---|---|---|
| Zn1–N43 | 2.000(3) | Zn1–O1W | 2.122(3) |
| Zn1–N32 | 2.027(3) | Zn1–N11 | 2.179(3) |
| Zn1–N21 | 2.071(3) | | |
| | | | |
| N32–Zn1–N11 | 90.05(13) | N21–Zn1–O1W | 89.70(13) |
| N21–Zn1–N11 | 78.18(15) | N43–Zn1–N11 | 94.63(13) |
| O1W–Zn1–N11 | 166.75(14) | N43–Zn1–N32 | 112.27(13) |
| N43–Zn1–O1W | 95.67(11) | N43–Zn1–N21 | 116.96(12) |
| N32–Zn1–O1W | 93.74(12) | N32–Zn1–N21 | 130.02(12) |

**Symmetry codes for 3:** #1 $-x + 1/2, -y + 3/2, -z + 1$, #2 $-x + 1/2, -y + 1/2, -z + 1$.

**Table S5.** Summary of SHAPE analysis for compound **1.**

| Metal | label | shape | symmetry | Distortion(τ) |
|---|---|---|---|---|
| | HP-7 | Heptagon | $D_{7h}$ | 31.886 |
| | HPY-7 | Hexagonal pyramid | $C_{6v}$ | 20.086 |
| | **PBPY-7** | **Pentagonal bipyramid** | **$D_{5h}$** | **1.916** |
| Cd1 | COC-7 | Capped octahedron | $C_{3v}$ | 5.877 |
| | CTPR-7 | Capped trigonal prism | $C_{2v}$ | 4.147 |
| | JPBPY-7 | Johnson pentagonal bipyramid J13 | $D_{5h}$ | 5.055 |
| | JETPY-7 | Johnson elongated triangular pyramid J7 | $C_{3v}$ | 19.941 |

**Table S6.** Summary of SHAPE analysis for compound **2.**

| Metal | label | shape | symmetry | Distortion(τ) |
|---|---|---|---|---|
| Cd | OP-8 | Octagon | $D_{8h}$ | 28.687 |
| | HPY-8 | Heptagonal pyramid | $C_{7v}$ | 25.853 |
| | **HBPY-8** | **Hexagonal bipyramid** | **$D_{6h}$** | **7.894** |
| | CU-8 | Cube | $O_h$ | 14.430 |
| | SAPR-8 | Square antiprism | $D_{4d}$ | 22.786 |
| | TDD-8 | Triangular dodecahedron | $D_{2d}$ | 20.7773 |
| | JGBF-8 | Johnson gyrobifastigium J26 | $D_{2d}$ | 12.965 |
| | JETBPY-8 | Johnson elongated triangular bipyramid J14 | $D_{3h}$ | 22.594 |

**Table S7.** Summary of SHAPE analysis for compound **3.**

| Metal | label | shape | symmetry | Distortion(τ) |
|---|---|---|---|---|
| Zn1 | PP-5 | Pentagon | $D_{5h}$ | 32.286 |
| | vOC-5 | Vacant octahedron | $C_{4v}$ | 4.312 |
| | **TBPY-5** | **Trigonal bipyramid** | **$D_{3h}$** | **1.029** |
| | SPY-5 | Spherical square pyramid | $C_{4v}$ | 2.739 |
| | JTBPY-6 | Johnson trigonal bipyramid J12 | $D_{3h}$ | 3.058 |

**Table S8.** Quantitative comparison of the principal π–π interactions in compounds **1**–**3**, derived from the PLATON analysis.

| Cg(I)-Cg(J) | Cg-Cg (Å) | Alpha (°) | CgI_Perp (Å) | Slippage (Å) |
|---|---|---|---|---|
| **Compound 1** | | | | |
| Cg(R3)-Cg(R3) | 3.563 | 0.00 | 3.330 | 1.267 |
| Cg(R1)-Cg(R5) | 3.724 | 13.25 | 3.327 | 2.000 |
| Cg(R3)-Cg(R4) | 3.808 | 0.54 | 3.333 | 1.831 |
| **Compound 2** | | | | |
| Cg(R2)-Cg(R2) | 4.215 | 0.00 | 3.947 | 1.478 |
| Cg(R3)-Cg(R3) | 3.795 | 0.00 | 3.385 | 1.715 |
| **Compound 3** | | | | |
| Cg(R4)-Cg(R4) | 3.596 | 0.00 | 3.343 | 1.325 |
| Cg(R1)-Cg(R3) | 3.634 | 9.07 | 3.535 | 0.567 |
| Cg(R2)-Cg(R4) | 3.666 | 1.05 | 3.370 | 1.427 |
| Cg(R6)-Cg(R6) | 3.693 | 0.00 | 3.567 | 0.957 |
| Cg(R6)-Cg(R7) | 3.856 | 2.78 | 3.545 | 1.434 |

**Notes:** Cg(I)/Cg(J) denote the centroids of the interacting rings. Alpha is the dihedral angle between the ring planes. Cg-Cg is the centroid-to-centroid distance. CgI_Perp is the perpendicular distance from Cg(I) to the plane of ring J. Slippage is the distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).

Ring labels used here: **Compound 1**: R1 benzene, R3 pyridyl, R4 benzene, R5 pyridyl; **Compound 2**: R2 benzene, R3 pyridyl; **Compound 3**: R1 tetrazole, R2/R4/R6 benzene, R3 tetrazole, R7 pyridyl.

**Table S9.** The main hydrogen bonds for compound **1-3**

| **Compound 1** | | | | | |
|---|---|---|---|---|---|
| Type | D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | <(DHA) (°) |
| | O11–H1...O14 | 0.81(2) | 1.74(2) | 2.5473(18) | 177(2) |
| | O1W–H1WA...O12 | 0.84(2) | 2.12(2) | 2.9256(18) | 161(2) |
| Intra | O1W–H1WB...N15 | 0.842(12) | 2.211(15) | 2.8728(18) | 136(2) |
| Intra | C11–H11A...O13 | 0.93 | 2.32 | 2.9711(19) | 126 |
| Intra | C22–H22A... O1W | 0.93 | 2.58 | 3.224(2) | 127 |

| **Compound 2** | | | | | |
|---|---|---|---|---|---|
| Type | D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | <(DHA) (°) |
| | O1W–H1WA...N23 | 0.837(16) | 2.14(2) | 2.914(3) | 153(2) |
| | O1W–H1WB...O24 | 0.834(16) | 1.889(16) | 2.717(3) | 172(3) |
| | O23 H27A...N24 | 0.74(4) | 1.95(4) | 2.653(3) | 158(4) |
| | O22–H28A...O21 | 1.05(9) | 1.54(9) | 2.586(3) | 174(9) |
| Intra | C22–H22A...O22 | 0.93 | 2.43 | 2.740(3) | 100 |
| Intra | C22–H22A...N21 | 0.93 | 2.52 | 2.847(3) | 101 |
| | C24–H24A...O23 | 0.93 | 2.40 | 3.283(3) | 160 |

| Compound 3 | | | | | |
|---|---|---|---|---|---|
| Type | D–H···A | D–H (Å) | H···A (Å) | D···A (Å) | <(DHA) (°) |
| | O3W–3WA...O1W | 0.846(17) | 2.556(17) | 3.129(7) | 125.9(15) |
| | O3W–H3WB...O24 | 0.849(13) | 2.28(3) | 2.803(6) | 120(2) |
| | O3W–H3WB...N12 | 0.849(13) | 2.124(17) | 2.873(6) | 147(3) |
| | O2W–H2WA...O4W | 0.85(3) | 2.275(18) | 2.853(9) | 126(3) |
| | O2W–H2WB...O4W | 0.848(18) | 2.47(3) | 3.014(9) | 122(2) |
| | O1W–H1WB...O3W | 0.850(17) | 2.36(2) | 3.129(7) | 152(2) |
| | O4W–H4WA...O24 | 0.85(3) | 1.99(3) | 2.827(8) | 168(4) |
| | O4W–H4WB...O5W | 0.85(2) | 2.52(3) | 2.939(11) | 111(3) |
| | O6W–H6WA...O5W | 0.849(18) | 2.04(2) | 2.829(13) | 155(3) |
| | O5W–H5WA...O23 | 0.849(19) | 1.962(19) | 2.757(9) | 156(2) |
| | C11–H11A...N23 | 0.93 | 2.46 | 3.381(7) | 172 |
| | C34–H34A...O3W | 0.93 | 2.59 | 3.127(7) | 117 |

**Table S10.** The corresponding CIE coordinates (x, y), CRI and CCT values for **1** under different excitation wavelengths.

| $\lambda_{ex}$ / nm | CIE (x, y) | CRI | CCT |
|---|---|---|---|
| 300 | (0.219 0.232) | 86 | 3349 |

| | | | |
|---|---|---|---|
| 320 | (0.232 0.212) | 93 | 5863 |
| 340 | (0.236 0.222) | 94 | 3841 |
| 360 | (0.247 0.246) | 92 | 1649 |
| 380 | (0.263 0.313) | 81 | 2784 |
| 400 | (0.284 0.366) | 75 | 3944 |

**Table S11.** Fluorescence decay parameters of compound **1-3.**

| Compound | $\lambda_{em}$ / nm | $\tau_1$ (ns) | $A_1$ | $\tau_2$ (ns) | $A_2$ | $\tau$ (ns) |
|---|---|---|---|---|---|---|
| **1** | 500 | 1.39 | 0.52 | 7.24 | 0.48 | 4.2 |
| **2** | 485 | 6.82 | 0.51 | 15.89 | 0.49 | 11.3 |
| **3** | 500 | 3.45 | 0.42 | 10.20 | 0.58 | 7.37 |

The lifetime data were processed according to the literature method.[1] Decay in the fluorescence intensity ($I$) with time ($\tau$) was fitted by a double-exponential function: $I = A_1 \exp(-t / \tau_1) + A_2 \exp(-t / \tau_2)$ (1), where $\tau_1$ and $\tau_2$ are the lifetimes of shorter- and longer-lived species, respectively, and $A_1$ and $A_2$ are their respective amplitudes. The weighted mean lifetime ($< \tau >$) was calculated according to Equation (2): $< \tau > = (A_1 \tau_1 + A_2 \tau_2) / (A_1 + A_2)$.

(1). Qin, A.; Jim, C. K.; Tang, Y.; Lam, J. W.; Liu, J.; Mahtab, F.; Gao, P.; Tang, B. Z. *J. Phys. Chem. B*, 2008, **112**, 9281–9288.

**Table S12**. Solid-state photoluminescence quantum yields (PLQYs) of compounds **1**–**3** measured under 400 nm excitation.

| **Compound** | **Excitation wavelength / nm** | **PLQY/%** |
|---|---|---|
| **1** | 400 | 5.53 |
| **2** | 400 | 6.65 |
| **3** | 400 | 5.21 |

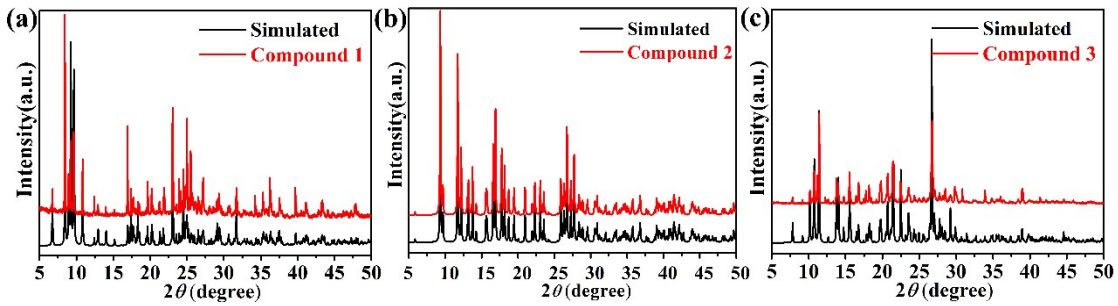


**Figure S1**. Comparison of experimental PXRD patterns for compound **1** (a), compound **2** (b) and compound **3** (c) to their simulated ones from single-crystal X-ray data.

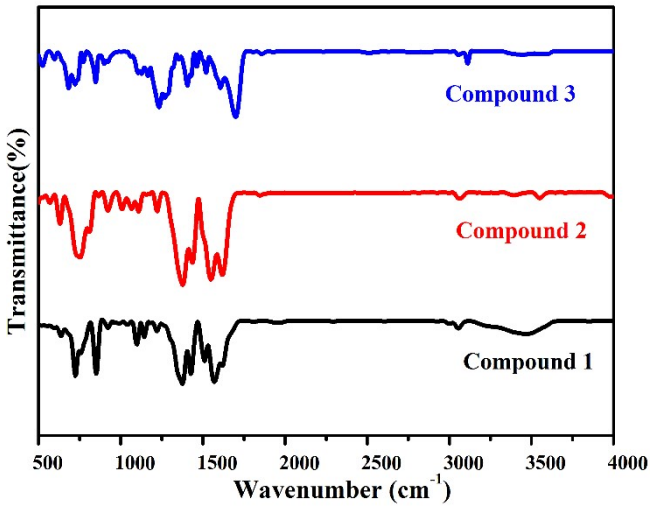


**Figure S2.** FT-IR curves for compound **1-3**

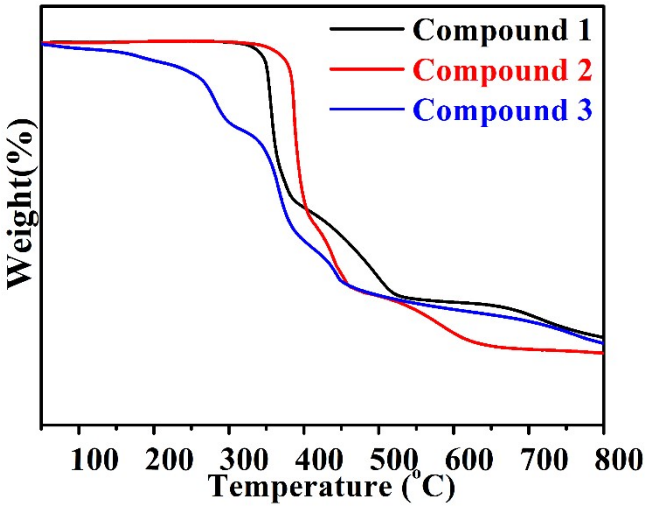


**Figure S3.** TGA curves for compound **1-3**.

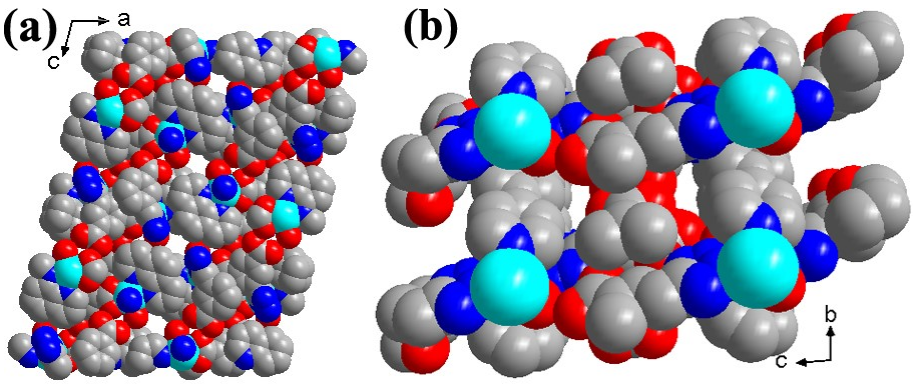


**Figure S4**. 3D supramolecular framework of compound **1** (a) and compound **2** (b).

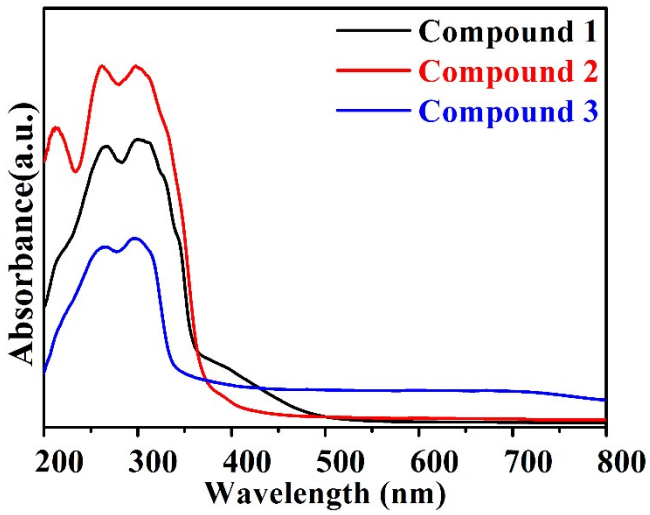


**Figure S5.** The solid-state UV-vis absorption spectra of compound **1**–**3** at room temperature.

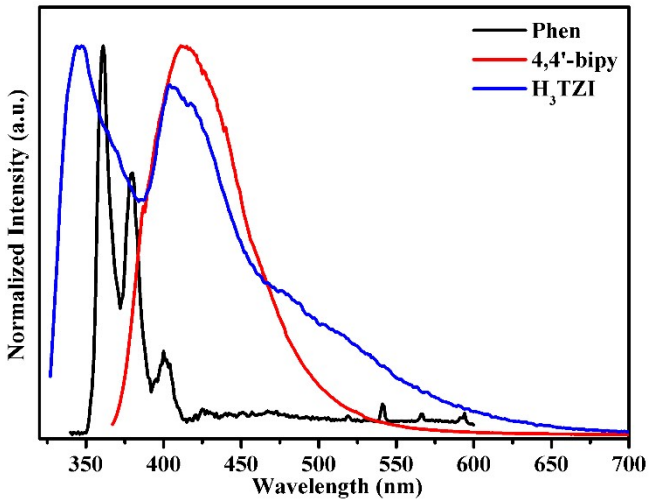


**Figure S6.** The photoluminescence spectra of ligands Phen, 4,4 '-bipy and $H_3TZI$ when excited at 320 nm.

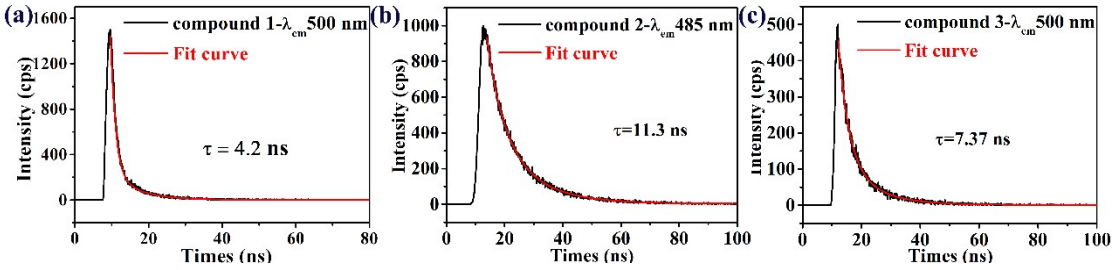


**Figure S7.** Fluorescence decay plot of compound **1-3**.

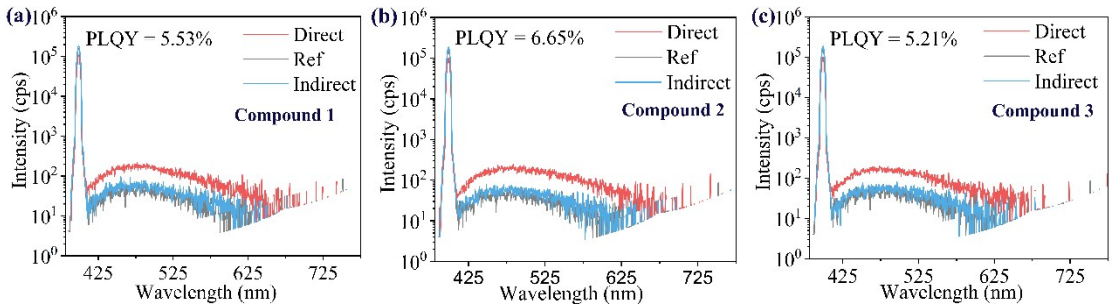


**Figure S8.** Quantum yield plot of compound **1-3** under 400 nm excitation and the emission wavelength is 500 nm, 485 nm and 500 nm, respectively.