***Supporting Information***

# Highly photo- and triboluminescent lanthanide(III) coordination polymers based on diphosphine dioxides containing azaheterocyclic linkers

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**Table S1.** Selected bond lengths and angles for CPs **1**, **4**, and **6**.

| **1** | | **4** | | **6** | |
|---|---|---|---|---|---|
| Bond | Bond lengths (Å) | Bond | Bond lengths (Å) | Bond | Bond lengths (Å) |
| Eu1–O1 | 2.347 (2) | Tb1–O1 | 2.290(2) | Tb1–O1 | 2.334(2) |
| Eu1–O2$^{i}$ | 2.370(2) | Tb1–O2 | 2.309(2) | Tb1–O2$^{i}$ | 2.327(2) |
| Eu1–O1_1 | 2.399(2) | Tb1–O1_1 | 2.374(3) | Tb1–O1_1 | 2.384(2) |
| Eu1–O2_1 | 2.497(2) | Tb1–O2_1 | 2.402(2) | Tb1–O2_1 | 2.399(2) |
| Eu1–O1_2 | 2.407(2) | Tb1–O1_2 | 2.365(3) | Tb1–O1_2 | 2.262(16) |
| Eu1–O2_2 | 2.463(2) | Tb1–O2_2 | 2.413(3) | Tb1–O2_2 | 2.276(15) |
| Eu1–O1_3 | 2.394(2) | Tb1–O1_3 | 2.425(2) | Tb1–O1_3 | 2.364(4) |
| Eu1–O2_3 | 2.402(2) | Tb1–O2_3 | 2.363(3) | Tb1–O2_3 | 2.416(4) |
| Eu1–N2C$^{i}$ | 2.866(2) | | | Tb1–O1_4 | 2.270(11) |
| | | | | Tb1–O2_4 | 2.350(11) |
| | | | | Tb1–O1_5 | 2.383(6) |
| | | | | Tb1–O2_5 | 2.415(6) |
| P1–O1 | 1.490(2) | P1–O1 | 1.497(2) | P1–O1 | 1.492(2) |
| P1–C1A | 1.789(2) | P1–C1A | 1.792(4) | P1–C1A | 1.787(4) |
| P1–C1B | 1.790(2) | P1–C1B | 1.788(4) | P1–C1B | 1.796(4) |
| P1–C1C | 1.824(2) | P1–C1C | 1.837(4) | P1–C1C | 1.821(3) |
| P2–O2 | 1.497(2) | P2–O2 | 1.501(3) | P2 –O2 | 1.497(2) |
| P2–C1D | 1.785(3) | P2–C1D | 1.795(4) | P2–C1D | 1.788(4) |
| P2–C4C | 1.820(2) | P2–C3C | 1.832(4) | P2–C4C | 1.823(3) |
| P2 –C1E | 1.787(3) | P2–C1E | 1.788(4) | P2–C1E | 1.790(4) |
| | | | | | |
| Angle | Angle size (°) | Angle | Angle size (°) | Angle | Angle size (°) |
| O1–Eu1–O2$^{i}$ | 75.97(5) | O1–Tb1–O2$^{i}$ | 81.39(9) | O1–Tb1–O2$^{i}$ | 145.54(9) |
| O1–Eu1–O2_2 | 74.56(5) | O1–Tb1–O2_1 | 75.62(9) | O1–Tb1–O2_1 | 73.54(9) |
| O1–Eu1–O1_2 | 143.53(6) | O1–Tb1–O1_1 | 114.40(9) | O1–Tb1–O1_1 | 143.13(9) |
| O1–Eu1–O1_1 | 85.66(5) | O1–Tb1–O2_2 | 142.38(9) | O1–Tb1–O2_3 | 78.82(13) |
| O1–Eu1–O2_1 | 68.52(5) | O1–Tb1–O1_2 | 146.03(9) | O1–Tb1–O1_3 | 83.77(11) |
| O1–Eu1–O1_3 | 90.69(6) | O1–Tb1–O2_3 | 79.98(9) | O1–Tb1–O2_4 | 81.4(3) |
| O1–Eu1–O2_3 | 138.88(5) | O1–Tb1–O1_3 | 77.14(8) | O1–Tb1–O1_5 | 70.92(17) |
| O2$^{i}$–Eu1–O2_2 | 78.62(5) | O2$^{i}$–Tb1–O2_1 | 80.54(8) | O1–Tb1–O2_5 | 105.73(18) |
| O2$^{i}$–Eu1–O1_2 | 92.81(6) | O2$^{i}$–Tb1–O1_1 | 142.36(9) | O2$^{i}$–Tb1–O2_1 | 140.45(9) |
| O2$^{i}$–Eu1–O1_1 | 77.73(5) | O2$^{i}$–Tb1–O2_2 | 73.95(9) | O2$^{i}$–Tb1–O1_1 | 70.62(9) |
| O2$^{i}$–Eu1–O2_1 | 132.06(5) | O2$^{i}$–Tb1–O1_2 | 108.62(9) | O2$^{i}$–Tb1–O1_3 | 104.10(11) |
| O2$^{i}$–Eu1–O1_3 | 145.85(5) | O2$^{i}$–Tb1–O2_3 | 148.15(9) | O2$^{i}$–Tb1–O2_3 | 72.62(12) |
| O2$^{i}$–Eu1–O2_3 | 136.18(5) | O2$^{i}$–Tb1–O1_3 | 79.27(8) | O2$^{i}$–Tb1–O2_4 | 73.2(3) |
| | | | | O2$^{i}$–Tb1–O1_5 | 82.41(18) |
| | | | | O2$^{i}$–Tb1–O2_5 | 84.39(18) |

i: x-1/2, -y+3/2, z-1/2 (complex **1**)
x-1/2, -y+1/2, z-1/2 (complex **4**)
-x+3/2, y-1/2, -z+3/2 (complex **6**)

**Table S2.** Selected bond lengths and angles for **3**

| **3** | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Bond | Bond lengths (Å) | Bond | Bond lengths (Å) | Bond | Bond lengths (Å) | Bond | Bond lengths (Å) | Bond | Bond lengths (Å) | Bond | Bond lengths (Å) |
| Eu11–O1_2$^{i}$ | 2.353(5) | Eu12–O1_1 | 2.353(5) | Eu21–O1_3 | 2.344(6) | Eu22–O2_3 | 2.345(5) | Eu31–O2_5 | 2.367(6) | Eu32–O1_5 | 2.356(6) |
| Eu11–O2_1 | 2.329(5) | Eu12–O2_2 | 2.342(5) | Eu21–O2_4$^{i}$ | 2.353(5) | Eu22–O1_4 | 2.387(5) | Eu31–O1_6$^{i}$ | 2.372(6) | Eu32–O2_6 | 2.339(5) |
| Eu11–O1_20 | 2.420(5) | Eu12–O1_23 | 2.492(5) | Eu21–O1_26 | 2.458(5) | Eu22–O1_29 | 2.49(3) | Eu31–O1_32 | 2.408(6) | Eu32–O1_35 | 2.421(7) |
| Eu11–O2_20 | 2.429(5) | Eu12–O2_23 | 2.409(5) | Eu21–O2_26 | 2.429(6) | Eu22–O2_29 | 2.43(2) | Eu31–O2_32 | 2.461(6) | Eu32–O2_35 | 2.476(6) |
| Eu11–O1_21 | 2.427(5) | Eu12–O1_24 | 2.389(5) | Eu21–O1_27 | 2.435(6) | Eu22–O1_30 | 2.464(5) | Eu31–O1_33 | 2.408(6) | Eu32–O1_36 | 2.388(6) |
| Eu11–O2_21 | 2.475(5) | Eu12–O2_24 | 2.415(5) | Eu21–O2_27 | 2.389(6) | Eu22–O2_30 | 2.381(5) | Eu31–O2_33 | 2.471(6) | Eu32–O2_36 | 2.417(6) |
| Eu11–O1_22 | 2.489(5) | Eu12–O1_25 | 2.408(5) | Eu21–O1_28 | 2.415(6) | Eu22–O1_31 | 2.39(2) | Eu31–O1_34 | 2.388(6) | Eu32–O1_37 | 2.414(6) |
| Eu11–O2_22 | 2.374(5) | Eu12–O2_25 | 2.465(5) | Eu21–O2_28 | 2.453(6) | Eu22–O2_31 | 2.42(4) | Eu31–O2_34 | 2.434(5) | Eu32–O2_37 | 2.458(6) |
| Eu11–N1_2$^{i}$ | 2.943(5) | Eu12–N1_1 | 2.863(6) | Eu21–N1_3 | 2.845(7) | Eu22–N1_4 | 2.953(6) | Eu31–N1_6$^{i}$ | 2.925(6) | Eu32–N1_5 | 2.874(7) |
| P1_1–O1_1 | 1.499(5) | P1_2–O1_2 | 1.496(5) | P1_3–O1_3 | 1.489 (6) | P1_4–O1_4 | 1.492 (5) | P1_5–O1_5 | 1.492 (6) | P1_6–O1_6 | 1.496 (6) |
| P1_1–C1A_1 | 1.792(8) | P1_2–C1A_2 | 1.784(7) | P1_3–C1A_3 | 1.785 (8) | P1_4–C1A_4 | 1.784 (8) | P1_5–C1B_5 | 1.786 (8) | P1_6–C1A_6 | 1.791 (9) |
| P1_1–C1B_1 | 1.784(7) | P1_2–C1B_2 | 1.789(7) | P1_3–C1B_3 | 1.766 (9) | P1_4–C1B_4 | 1.792 (8) | P1_5–C1C_5 | 1.826 (8) | P1_6–C1B_6 | 1.782 (9) |
| P1_1–C1C_1 | 1.830(7) | P1_2–C1C_2 | 1.841(7) | P1_3–C1C_3 | 1.834 (8) | P1_4–C1C_4 | 1.836 (8) | P1_5–C4_5 | 1.783 (9) | P1_6–C1C_6 | 1.820 (8) |
| P2_1–O2_1 | 1.495(5) | P2_2–O2_2 | 1.498(5) | P3_3–O2_3 | 1.483 (5) | P2_4–O2_4 | 1.485 (6) | P2_5–O2_5 | 1.497 (6) | P2_6–O2_6 | 1.485 (6) |
| P2_1–C1D_1 | 1.794(8) | P2_2–C1D_2 | 1.776(8) | P3_3–C1D_3 | 1.76 (3) | P2_4–C1D_4 | 1.790 (8) | P2_5–C1D_5 | 1.764 (9) | P2_6–C1D_6 | 1.785 (9) |
| P2_1–C1E_1 | 1.776(8) | P2_2–C1E_2 | 1.803(7) | P3_3–C1E_3 | 1.82 (4) | P2_4–C1E_4 | 1.803 (8) | P2_5–C1E_5 | 1.800 (8) | P2_6–C1E_6 | 1.768 (10) |
| P2_1–C3C_1 | 1.817(7) | P2_2–C3C_2 | 1.829(7) | P3_3–C3C_3 | 1.822 (7) | P2_4–C3C_4 | 1.809 (8) | P2_5–C3C_5 | 1.817 (8) | P2_6–C3C_6 | 1.814 (8) |
| | | | | | | | | | | | |
| Angle | Angle size (°) | Angle | Angle size (°) | Angle | Angle size (°) | Angle | Angle size (°) | Angle | Angle size (°) | Angle | Angle size (°) |
| O2_1–Eu11–N1_2$^{i}$ | 129.4(2) | O1_1–Eu12–N1_1 | 63.9(2) | O1_3–Eu21–N1_3 | 64.0(2) | O2_3–Eu22–N1_4 | 127.1(2) | O2_5–Eu31–N1_6$^{i}$ | 127.0(2) | O1_5–Eu32–N1_5 | 63.9(2) |
| O2_1–Eu11–O1_2$^{i}$ | 74.0(2) | O1_1–Eu12–O1_23 | 72.1(2) | O1_3–Eu21–O1_26 | 73.6(2) | O2_3–Eu22–O1_4 | 74.6(2) | O2_5–Eu31–O1_32 | 77.2(2) | O1_5–Eu32–O1_35 | 90.4(2) |
| O2_1–Eu11–O1_20 | 140.5(2) | O1_1–Eu12–O2_23 | 88.8(2 | O1_3–Eu21–O2_26 | 92.5(2) | O2_3–Eu22–O1_29 | 106.3(6) | O2_5–Eu31–O2_32 | 67.9(2) | O1_5–Eu32–O2_35 | 73.0(2) |
| O2_1–Eu11–O2_20 | 85.5(2) | O1_1–Eu12–O1_24 | 134.5(2) | O1_3–Eu21–O1_27 | 145.4(2) | O2_3–Eu22–O2_29 | 139.9(5) | O2_5–Eu31–O1_33 | 137.0(2) | O1_5–Eu32–O1_36 | 134.5(2) |
| O2_1–Eu11–O1_21 | 102.0(2) | O1_1–Eu12–O2_24 | 143.0(2) | O1_3–Eu21–O2_27 | 134.7(2) | O2_3–Eu22–O1_30 | 71.6(2) | O2_5–Eu31–O2_33 | 109.3(2) | O1_5–Eu32–O2_36 | 143.9(2) |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| O2_1–Eu11–O2_21 | 68.5(2) | O1_1–Eu12–O1_25 | 79.5(2) | O1_3–Eu21–O1_28 | 76.0(2) | O2_3–Eu22–O2_30 | 138.9(2) | O2_5–Eu31–O1_34 | 137.8(2) | O1_5–Eu32–O1_37 | 75.8(2) |
| O2_1–Eu11–O1_22 | 70.8(2) | O1_1–Eu12–O2_25 | 133.9(2) | O1_3–Eu21–O2_28 | 131.7(2) | O2_3–Eu22–O1_31 | 70.1(5) | O2_5–Eu31–O2_34 | 70.8(2) | O1_5–Eu32–O2_37 | 131.7(2) |
| O2_1–Eu11–O2_22 | 138.2(2) | O2_2–Eu12–O1_1 | 75.6(2) | O2_4$^{i}$–Eu21–O1_26 | 70.6(2) | O2_3–Eu22–O2_31 | 77.1(8) | O1_6$^{i}$–Eu31–O1_32 | 80.6(2) | O2_6–Eu32–O1_5 | 76.5(2) |

i: x, y-1, z

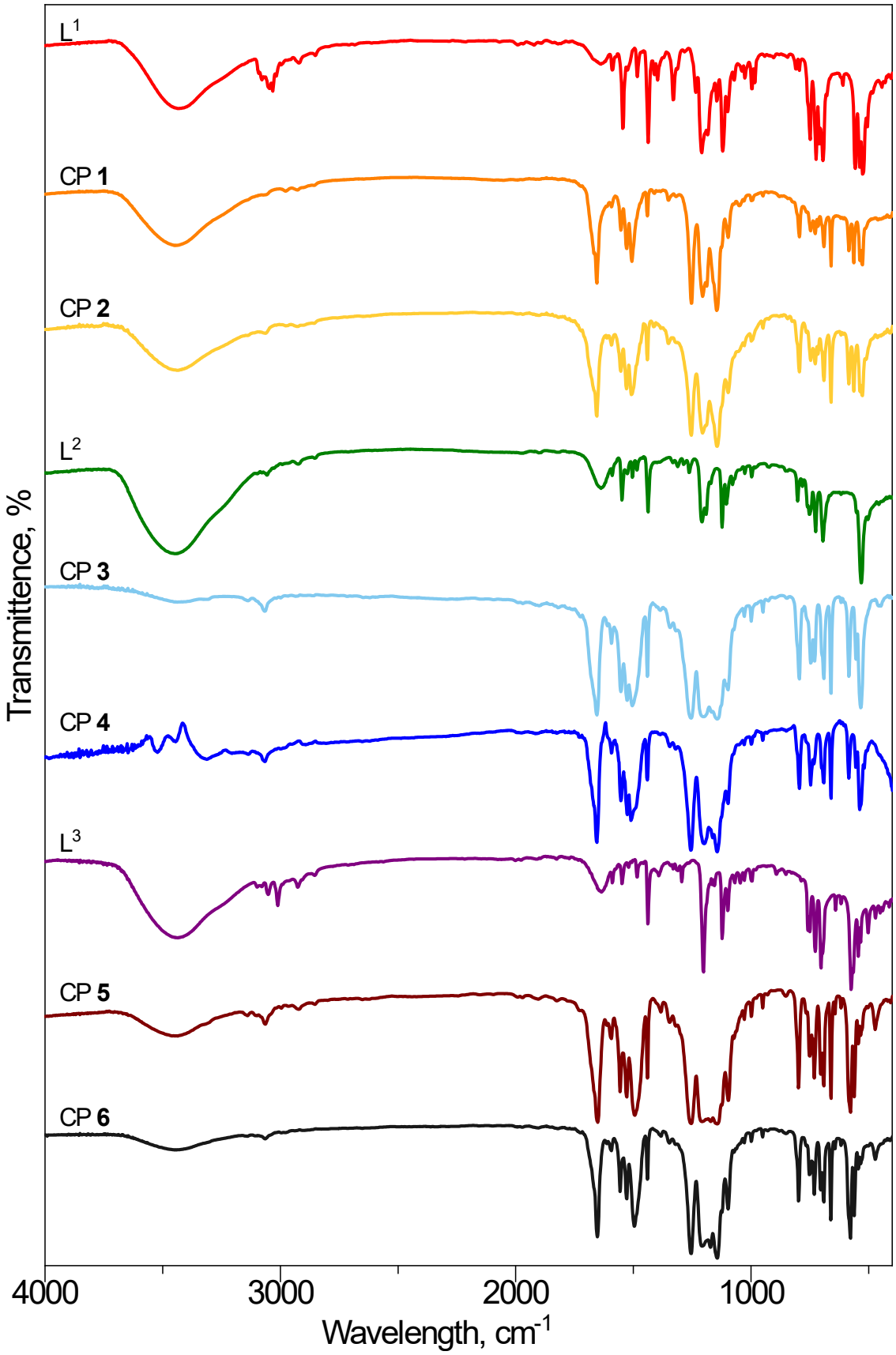


**Figure S1.** FT-IR spectra of compounds $L^{1–3}$ and CPs **1**–**6**.

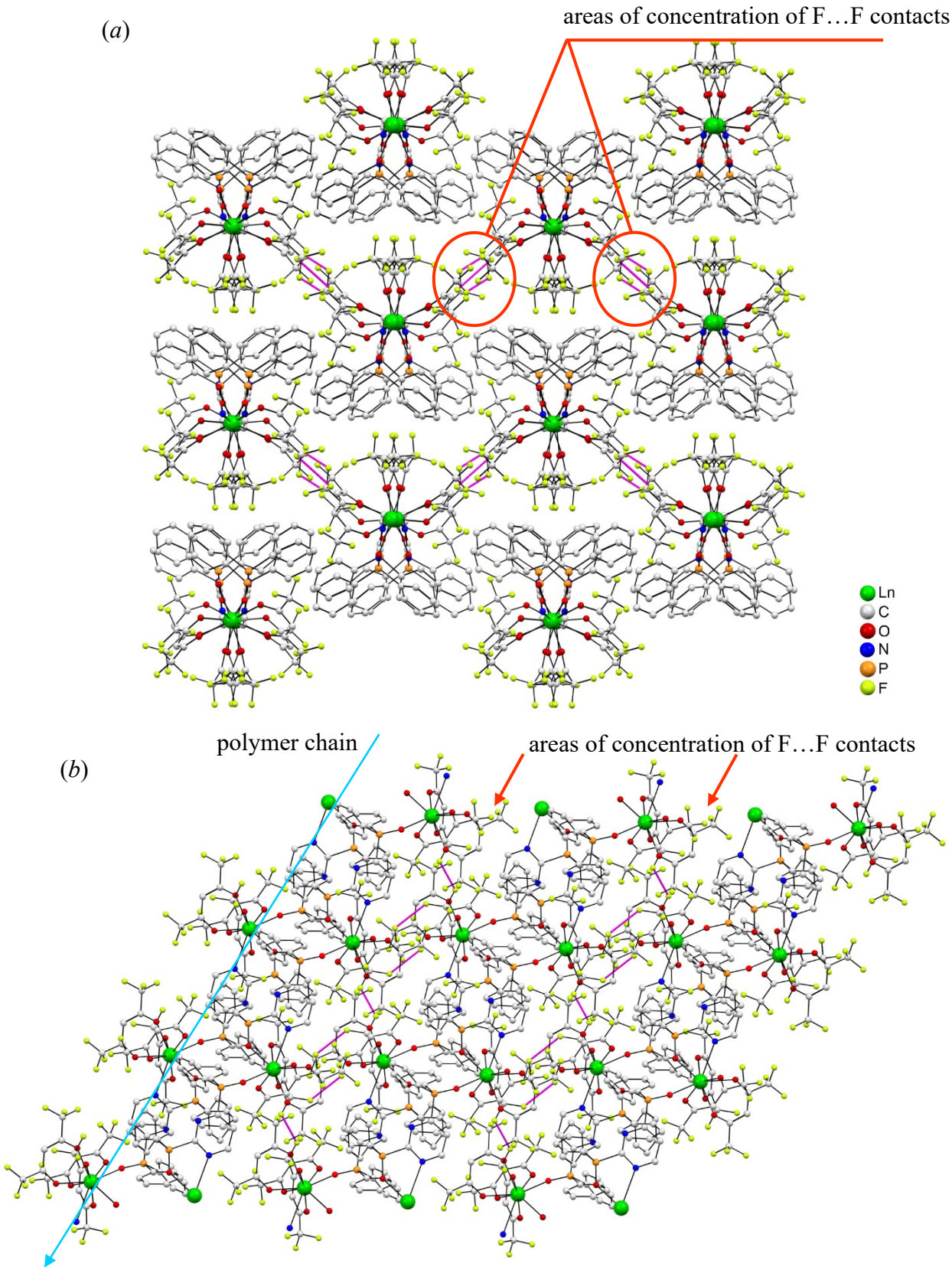


**Figure S2.** (*a*) Projection of the crystal structure of **1** perpendicular to the polymer chains and (*b*) view along the polymer chains (along the [010] direction) focused on F…F contacts (magenta). H atoms and disordered atom positions are omitted for clarity.

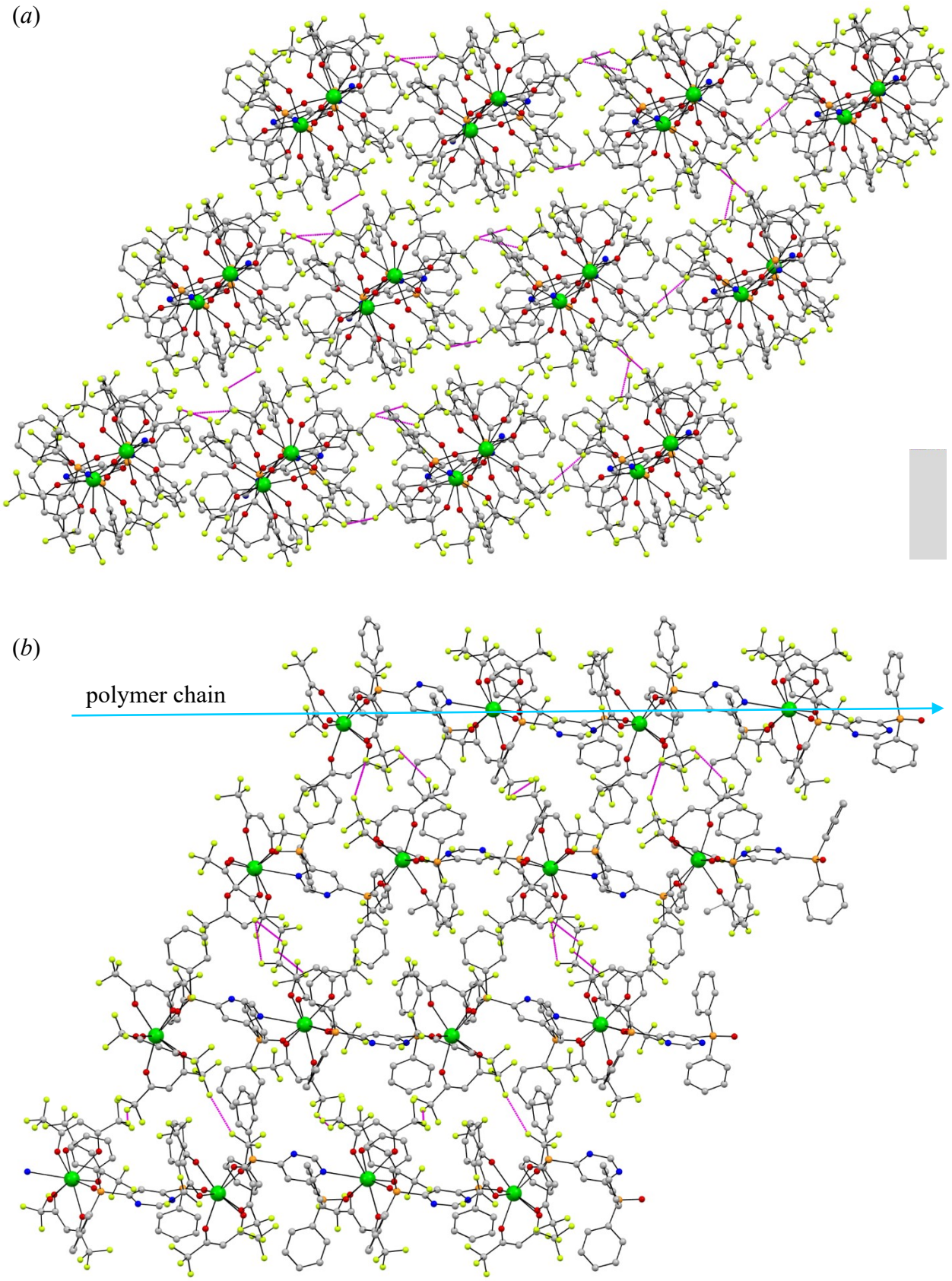


**Figure S3.** (*a*) Projection of the crystal structure of **3** perpendicular to the polymer chains (along the [010] direction) and (*b*) view along the polymer chain direction (along the [100] direction) focused on F…F contacts (magenta). H atoms and disordered atom positions are omitted for clarity.

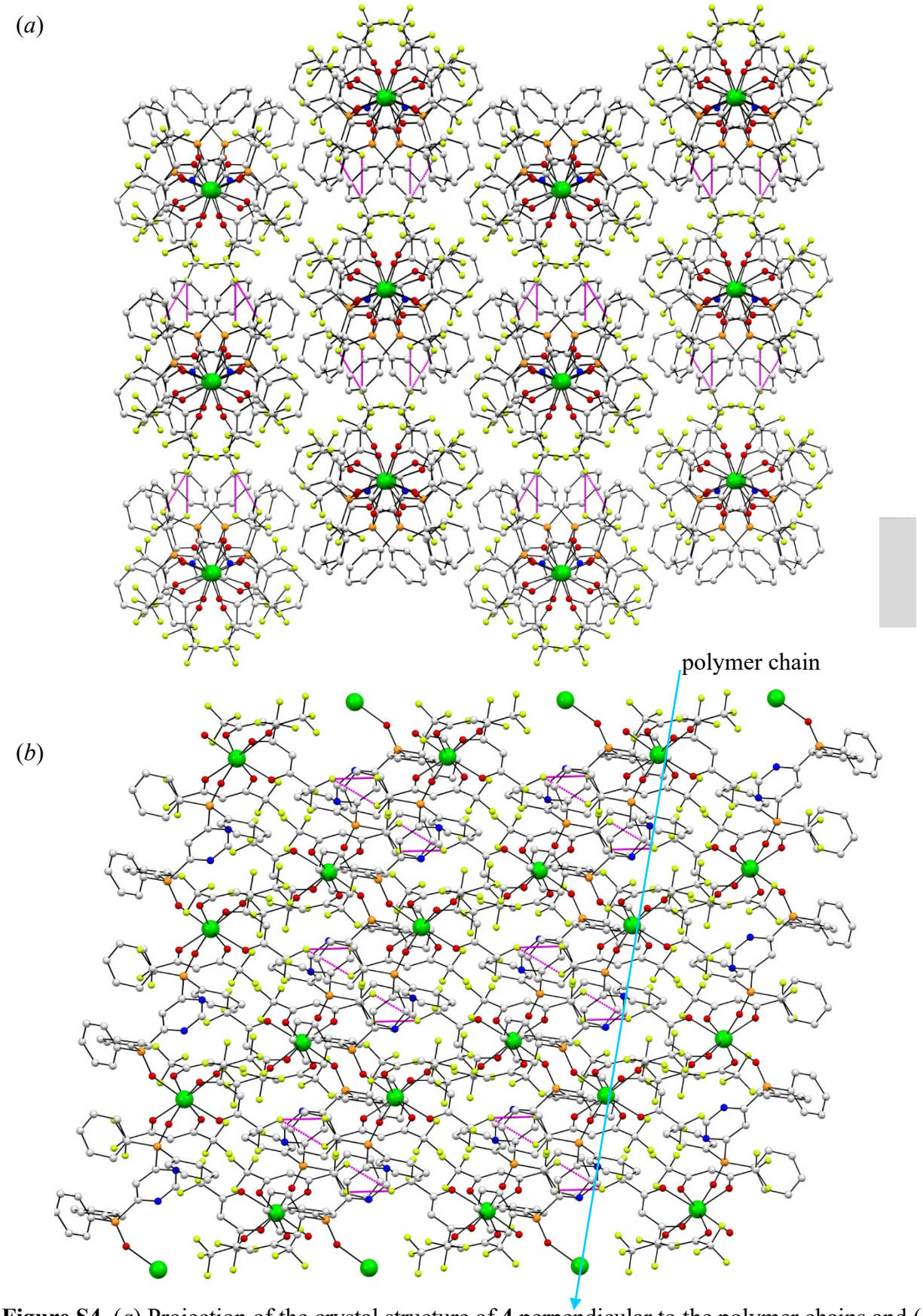


**Figure S4.** (*a*) Projection of the crystal structure of **4** perpendicular to the polymer chains and (*b*) view along the polymer chain direction (along the [010] direction) focused on F…F contacts (magenta). H atoms and disordered atom positions are omitted for clarity.

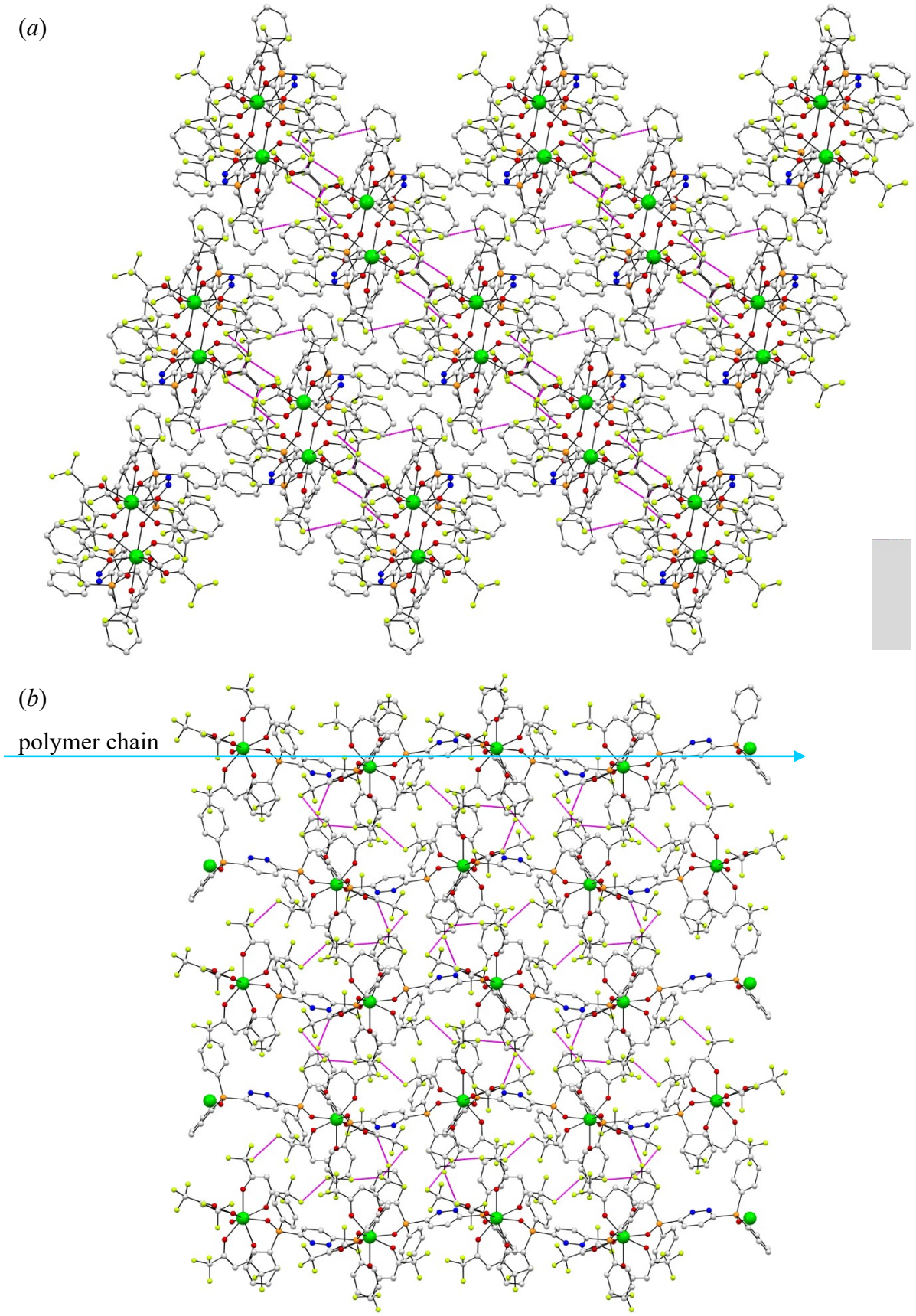


**Figure S5.** (*a*) Projection of the crystal structure of **6** perpendicular to the polymer chains (along the [010] direction) and (*b*) view along the polymer chain direction (along the [100] direction) focused on F…F contacts (magenta). H atoms and disordered atom positions are omitted for clarity.

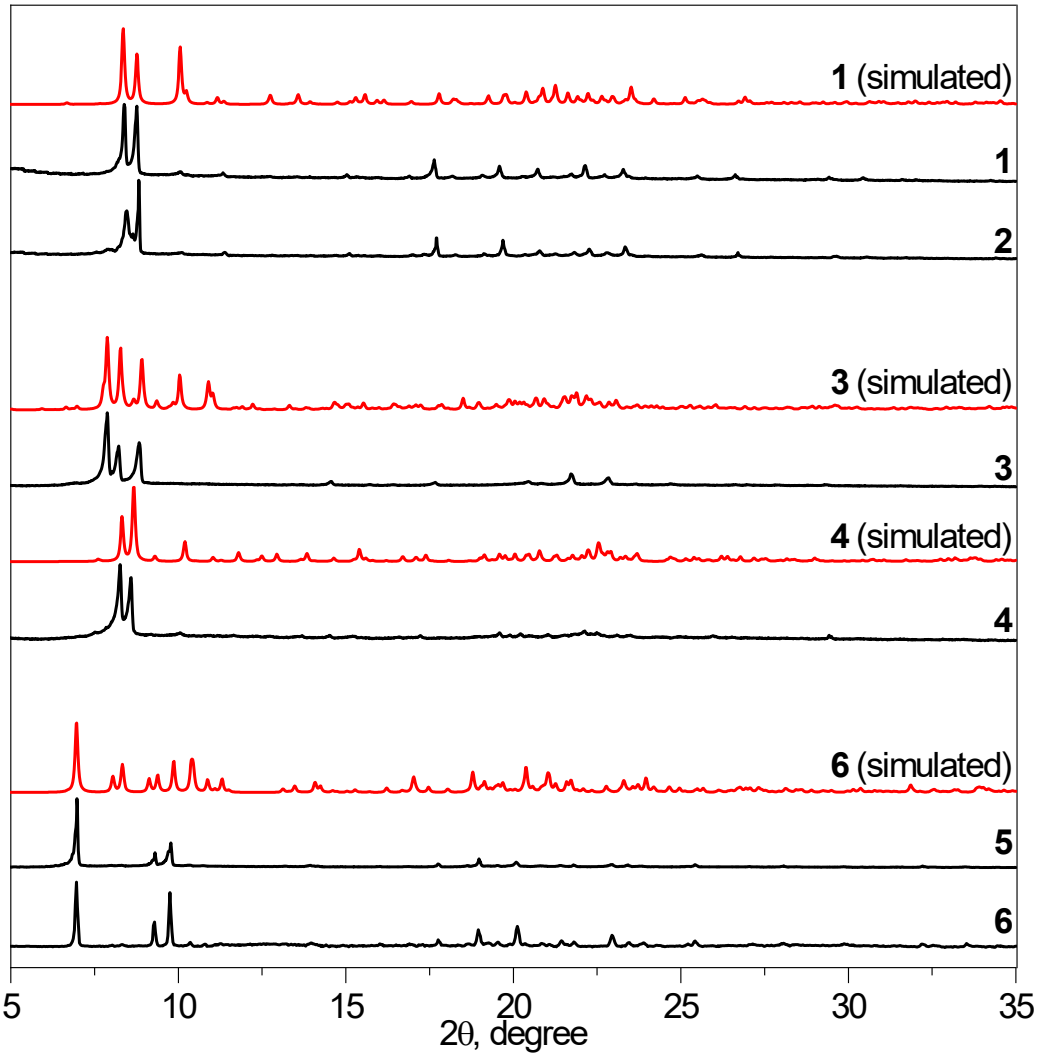


**Figure S6.** Simulated XRPD patterns of CPs **1**, **3**, **4** and **6** (red), and experimental ones of **1**−**6** (black).

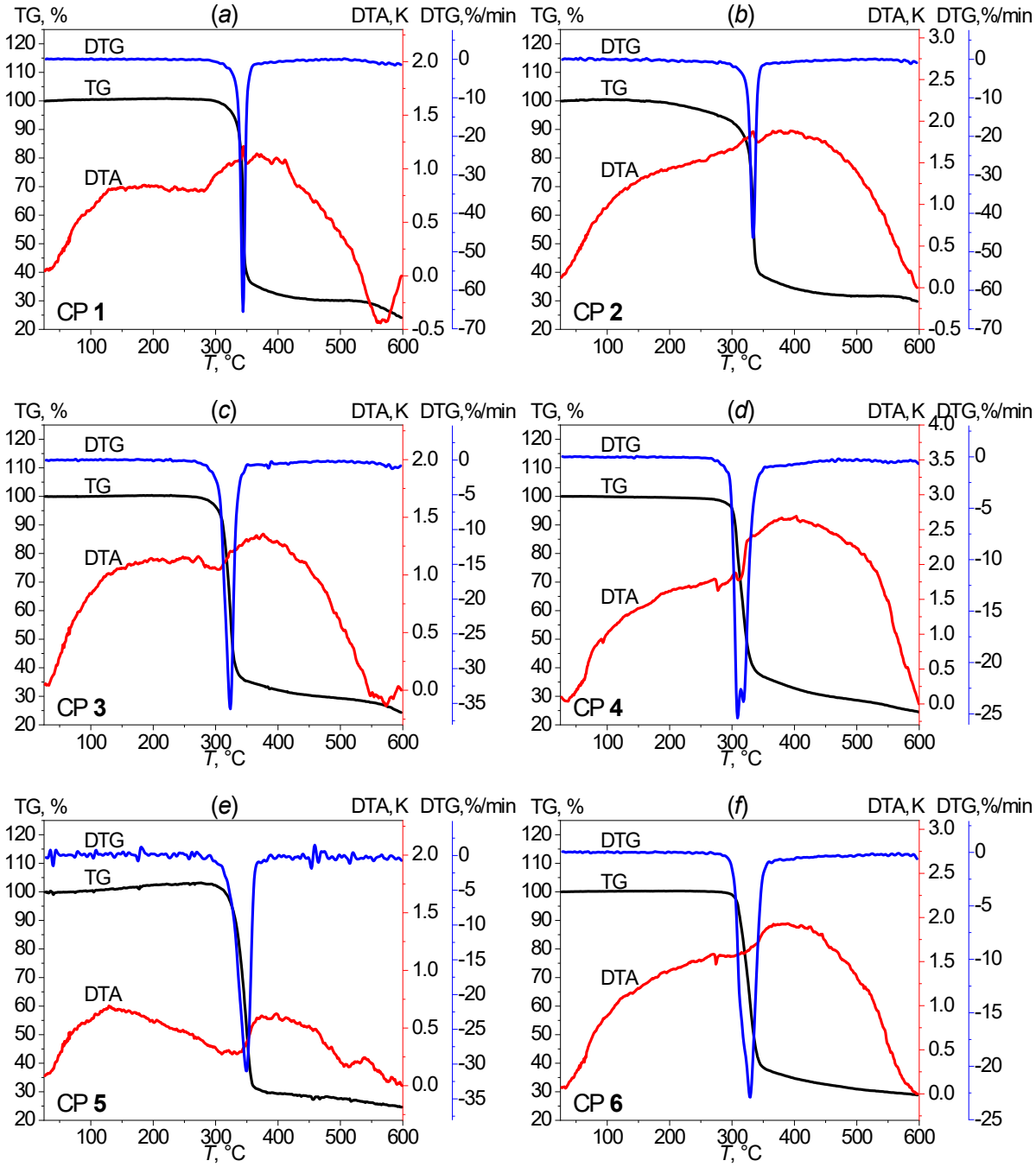


**Figure S7.** TG, DTA, and DTG of CPs **1** (*a*), **2** (*b*), **3** (*c*), **4** (*d*), **5** (*e*), and **6** (*f*).

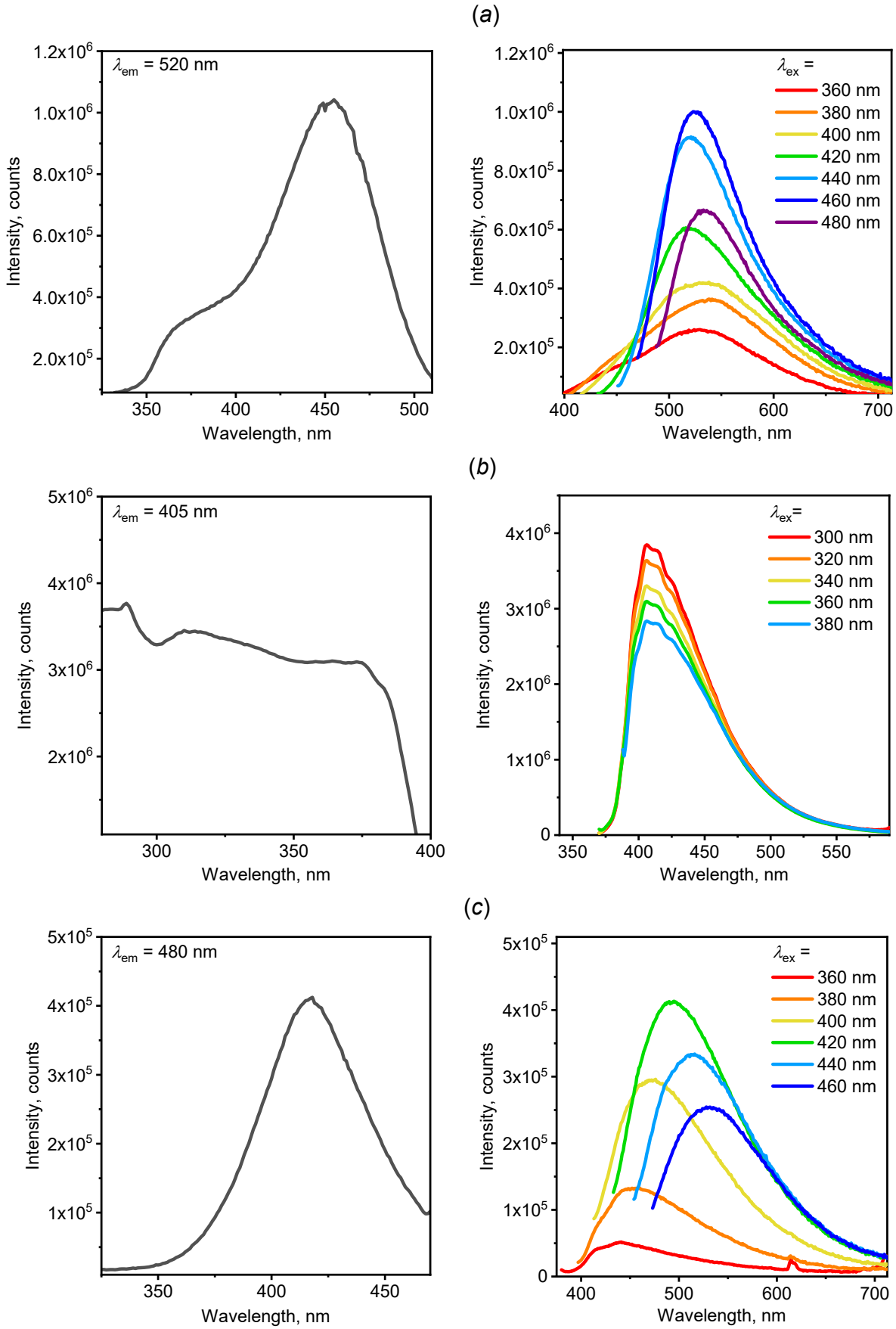


**Figure S8.** Excitation (left) and emission (right) spectra of $L^1$ (*a*), $L^2$ (*b*), and $L^3$ (*c*) in the solid state at 300 K.

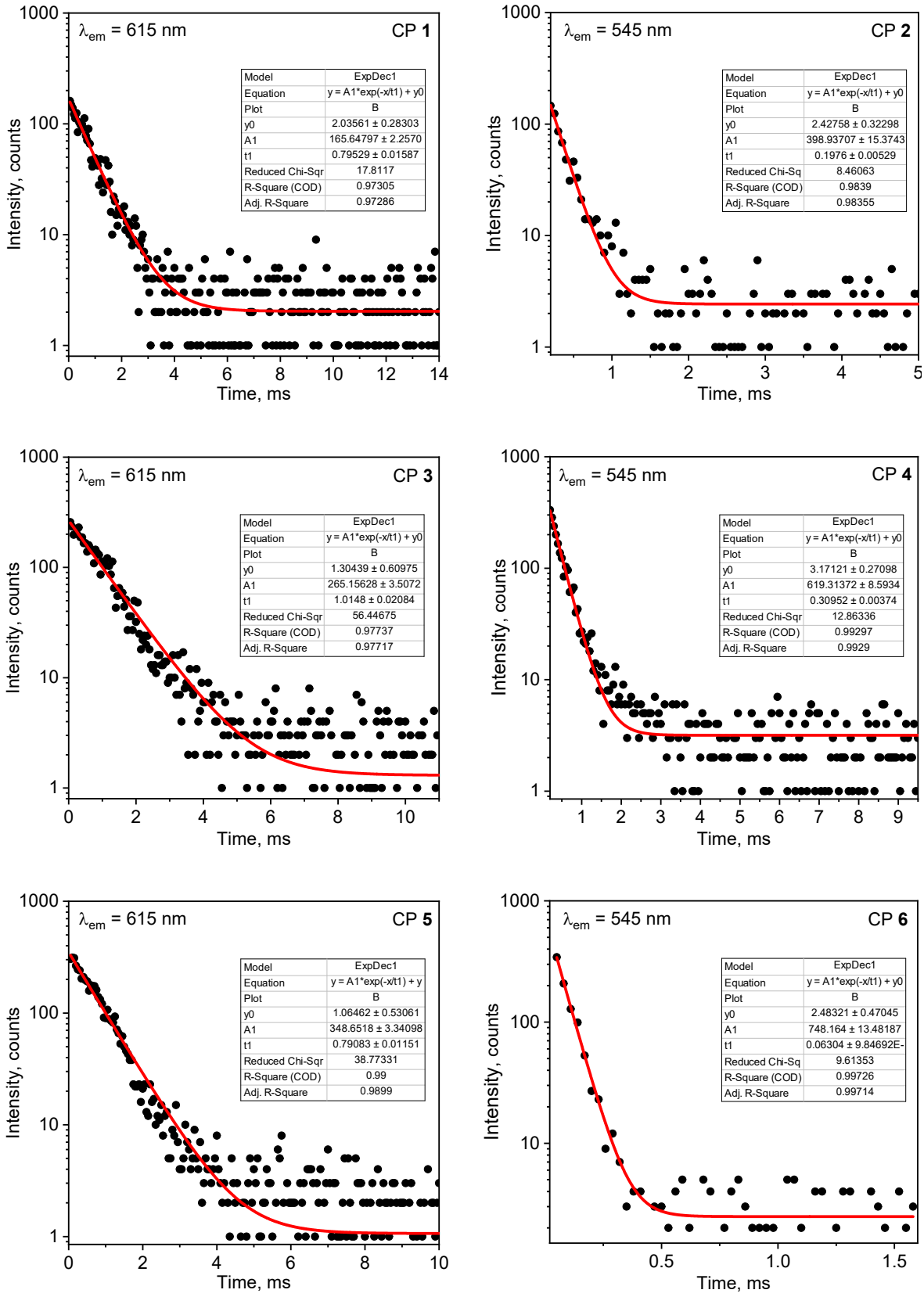


**Figure S9.** Kinetics of photoluminescence decay of CPs **1**–**6** in the solid state at 300 K ($\lambda_{ex}$ = 350 nm).

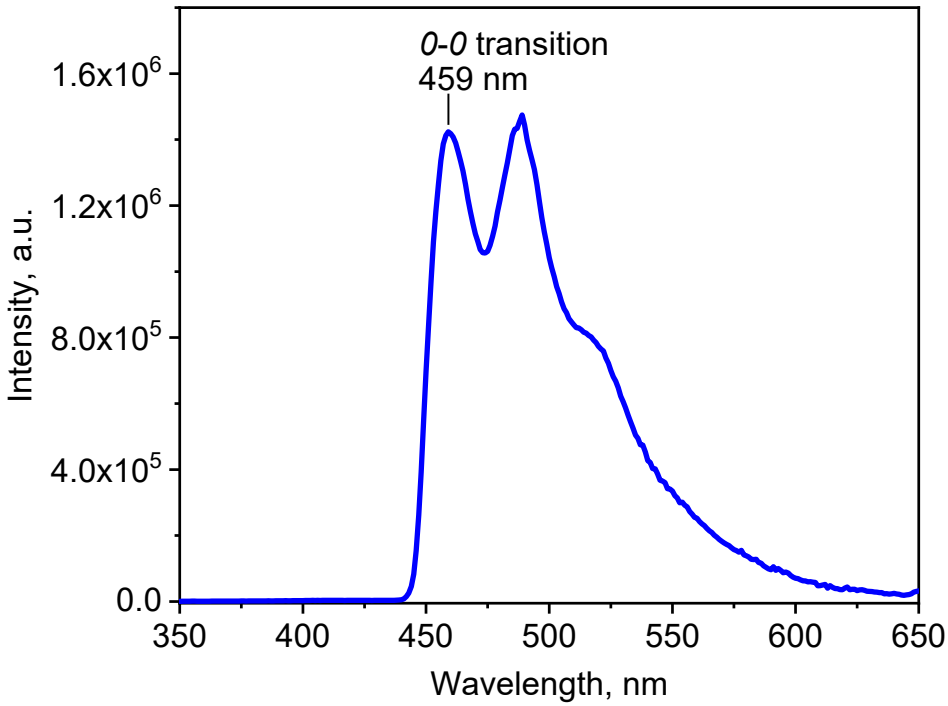


**Figure S10.** Solid-state emission spectrum of $[Gd(hfac)_3(H_2O)_2]$ at 77 K ($\lambda_{ex}$ = 338 nm).