A green luminescent 1-D helical tubular dipyrazol-bridged cadmium(II) complex: a coordination tube included in a supramolecular tube

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Electronic Supplementary Information:

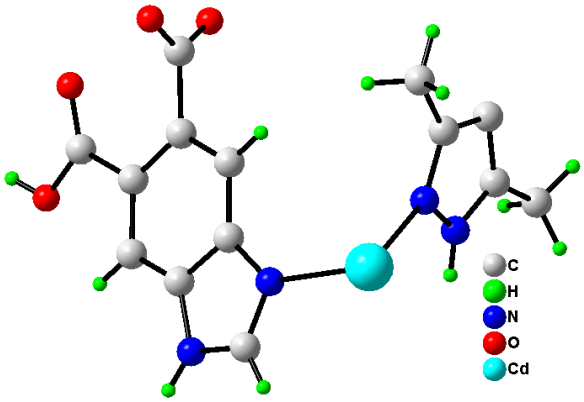


Fig. S1 Ball-stick view of the asymmetrical unit of **1.**

In the asymmetrical unit of **1**, there is 0.5 Cd^{2+} ion, 0.5 H_2Me_4bpz ligand and one H_2bidc^- anion, respectively.

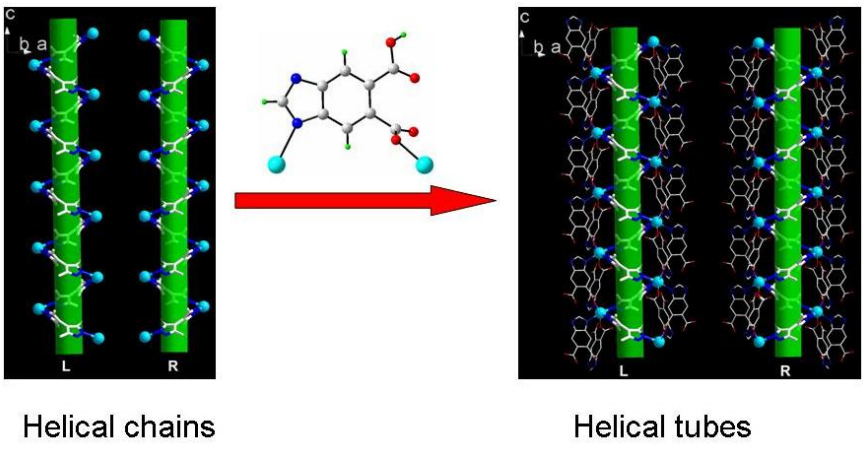


Fig. S2 View of the construction of the coordination helical tubes of **1** running along *c* axis.

The combination of bitopic H_2Me_4bpz with metal ions leads to two types of coordination helical chains with opposite chirality as shown in Fig 2, S2, possessing a 2_1 screw axis parallel to *c* with a pitch of 8.392(2) Å. The left- and right-handed helical chains are further weaved by H_2bidc^- anions through chelating the adjacent two Cd^{2+} ions parallel to *c* axis to make the elliptical helical tubes with opposite chirality.

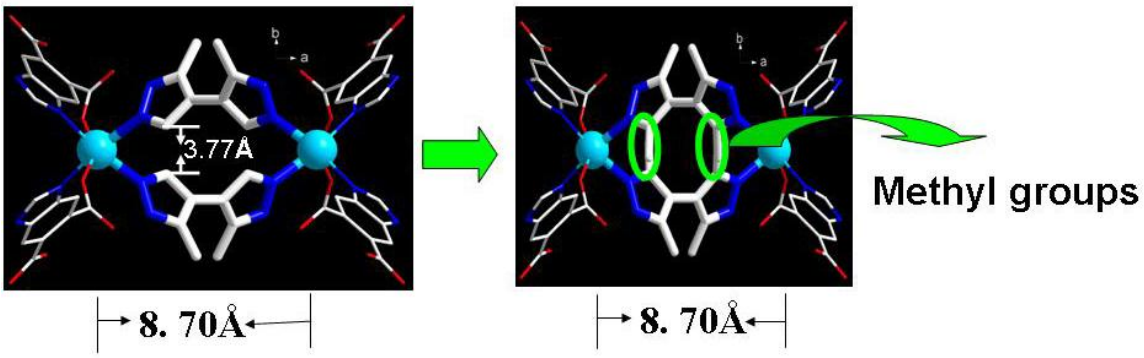


Fig. S3 The helical tube of **1** viewed along *c* axis.

The dimension of the coordination helical tube is about 3.77 Å× 8.70 Å. The one of the two methyl groups of H_2Me_4bpz point away from the Cd–H_2Me_4bpz helical chains and into the coordination helical tubes, then, the elliptical coordination tubes became the smaller approximate circular tubes.

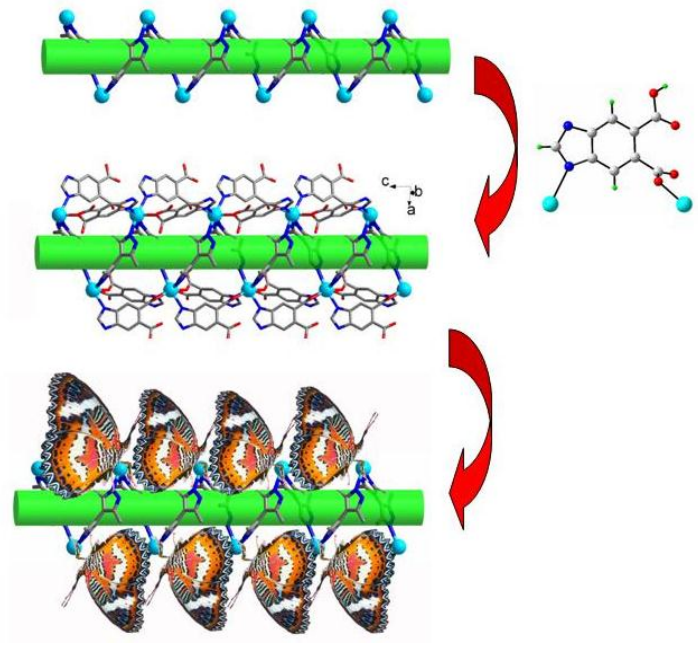


Fig. S4 The $[Cd_2(H_2bidc)_2]$ units like butterflies settling on the two sides of the tube.

The $[Cd_2(H_2bidc)_2]$ units like butterflies settled on the two sides of these tubes(Fig 1, S6).

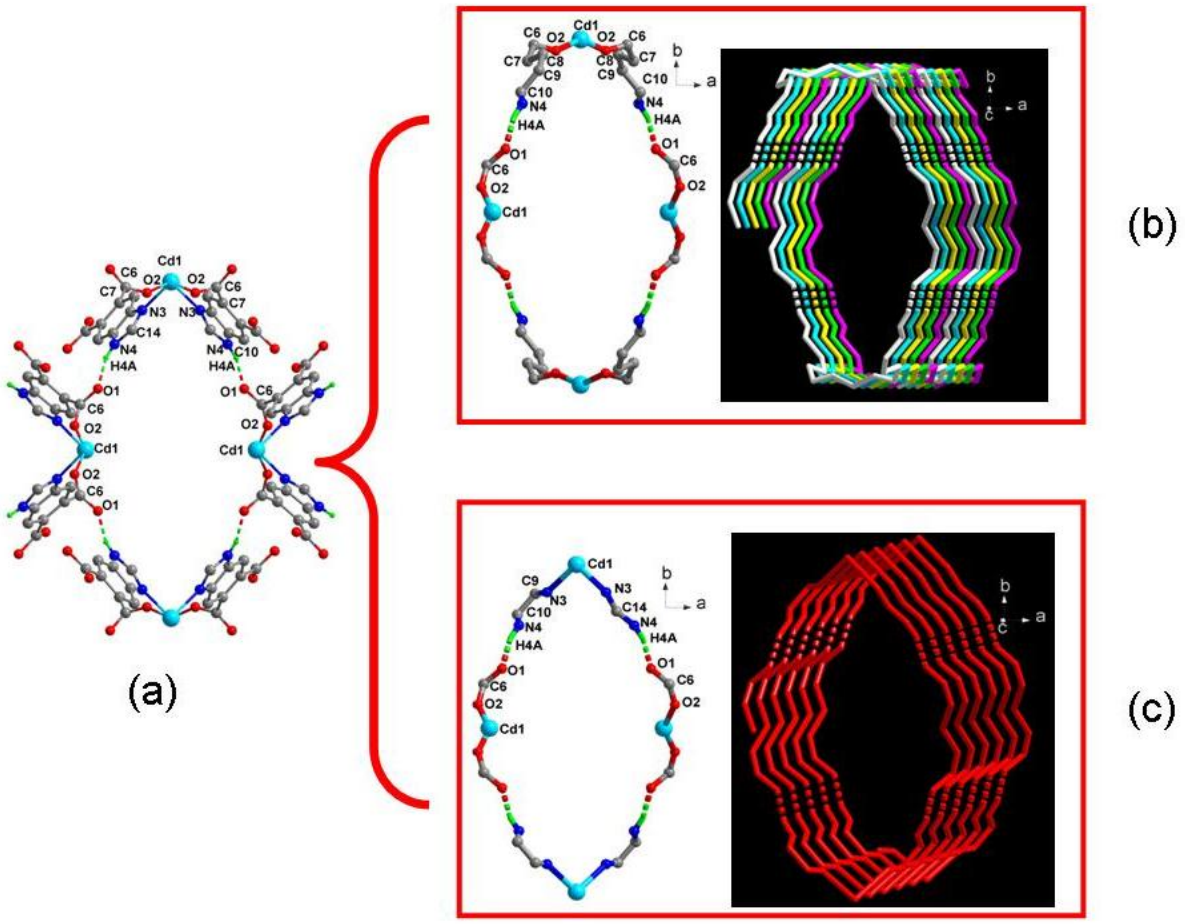


Fig. S5 The construction of the supramolecular helical tube in the combination of quintuple-helical- chain with single-helical-chain in the structure of **1**, (a) view of the supramolecular helical tube; (b) View of the supramolecular helical channels made of quintuple -helical-chain containing unclosed 48-membered ring along the [001] direction. Five helical chains of the quintuple -helical-chain are equivalent. [In the structure, four $[Cd(H_2bidc)]_n$ units are linked by N–H···O hydrogen bonds through two repeated -Cd1-O2-C6-O1···H4A-N4-C10-C9-C8-C7-C6-O2-Cd1-O2-C6-C7-C8-C9-C10-N4-H4A···O1-C6-O2- linkages to give rise to helical channels containing quintuple-helical-chain with the pitch of 8.392(2) Å along the *c*-axis; (c) View of the supramolecular helical channels made of single-helical-chain containing unclosed 34-membered ring along the [001] direction. [In the structure, the Cd atoms are linked by carboxyl groups of O1C6O2 and N–H···O hydrogen bonds through two repeated -Cd1-O2-C6-O1···H4A-N4-C10-C9-N3-Cd1-N3-C14-N4-H4A···O1-C6-O2- linkages to give rise to helical channels along the *c*-axis.

In compound **1**, H_2Me_4bpz and H_2bidc ligands both can act not only as a hydrogen-bond acceptor but also as a hydrogen bond-donor, so there are complex strong hydrogen bonds between them. Four $[Cd(H_2bidc)]_n$ units are linked by N–H···O hydrogen bonds (N···O: 2.659 Å and 2.895 Å)

to form a nano-size elliptical supramolecular helical channels with the dimension of 17.04 Å× 8.70 Å. The supramolecular helical channels, which are made of quintuple-helical chains, are further weaved by single-helical chains to make the tubular walls. As shown in Figure S7, the walls of the supramolecular helical tubular channels can be described as two parts: one part is the helical channels made of the quintuple-helical-chain containing five equivalent helical chains (Figure S7b), another is single-helical-chain (Figures S7c). The quintuple-helical-chain are further weaved by the single-helical-chain with the same helical orientation each other through sharing Cd vertices to form a unique helical tubular combination.

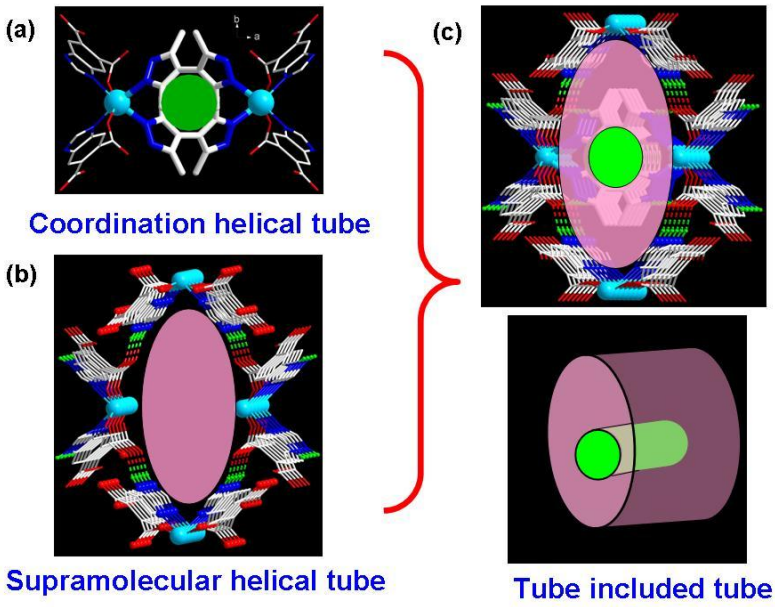


Fig. S6 The construction of the tube-in-tube structure viewed along *c* axis: (a) The coordination helical tube through Cd-N, Cd-O coordination bonds; (b) The supramolecular helical tube built from four $[Cd(H_2bidc)]_n$ units linked by N–H···O hydrogen bonds; (c) View of the coordination helical tube in the supramolecular helical tube.

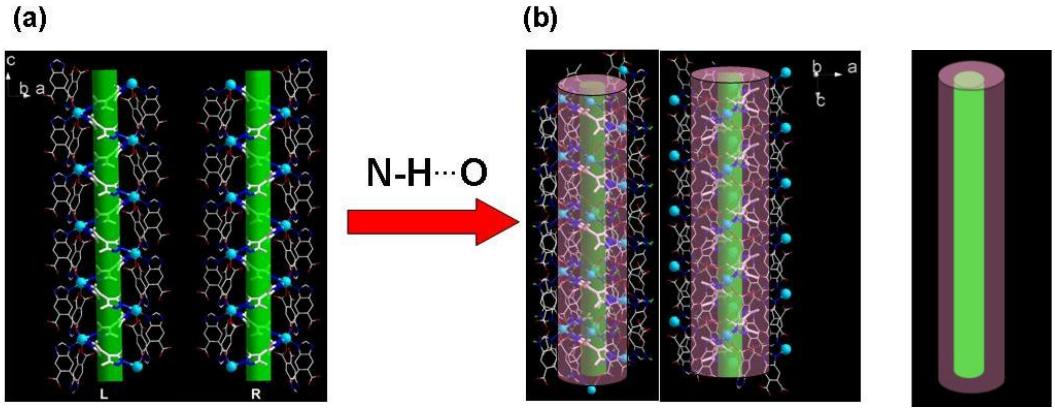
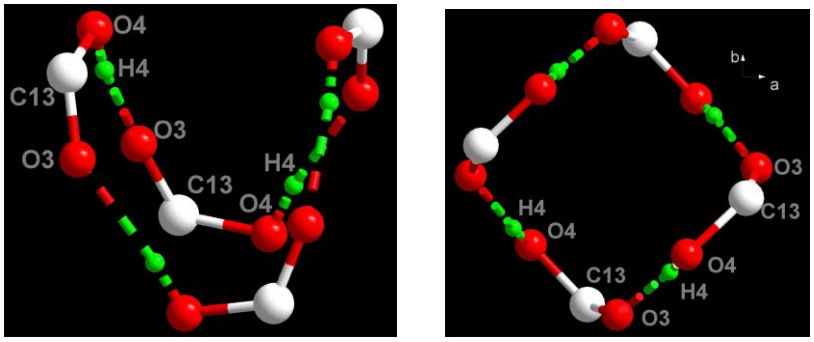


Fig. S7 The construction of the tube-in-tube structure viewed along *b* axis: (a) The coordination helical tube running along *c* axis; (b) The tube-in-tube structure.

Four $[Cd(H_2bidc)]_n$ units are linked by N–H···O hydrogen bonds(N···O: 2.659 Å and 2.895 Å) to form a nano-size elliptical supramolecular helical channels with the dimension of 17.04 Å× 8.70 Å, and the coordination helical tube with the same-handness is contained in it.



(a) **(b)**

Fig. S8 View of a 16-membered hydrogen bond ring in boat-like conformation comprised of four carboxylate groups by O–H···O hydrogen bonds.

The uncoordinated carboxylate groups point to the channels. Four carboxylate groups comprised a 16-membered ring in boat-like conformation by O–H···O hydrogen bonds(O···O: 2.595 Å).

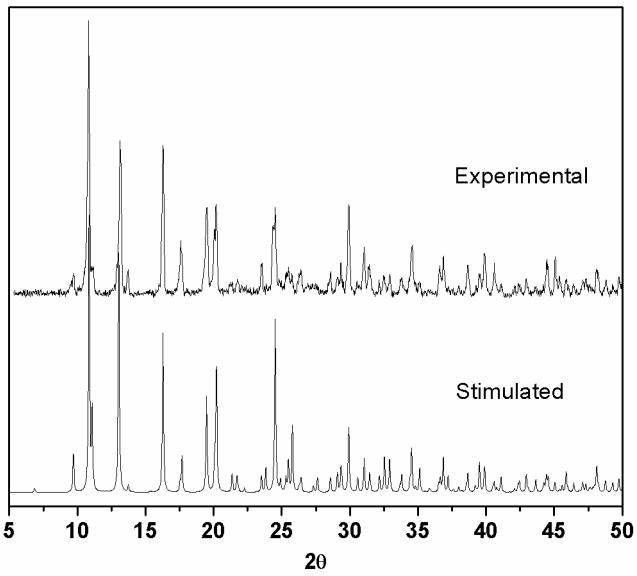


Fig. S9 The PXRD pattern of **1** and simulated respectively.

The good accordance of the experimental PXRD patterns with the simulated patterns indicates phase purity of **1**.

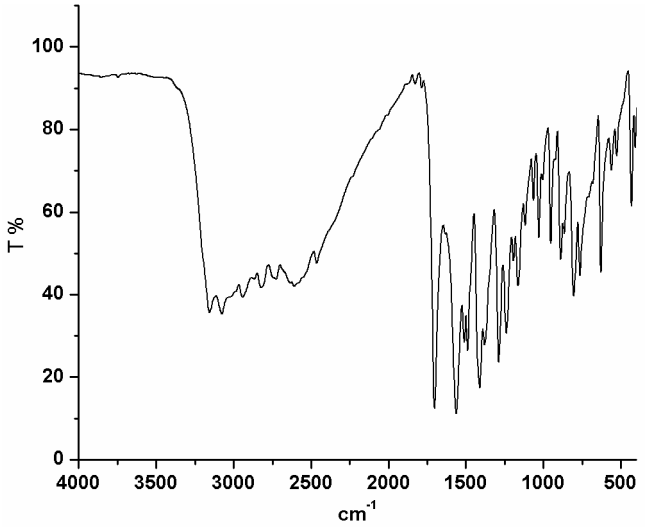


Fig. S10 IR spectrum of **1**

The IR spectrum (Fig S9) of **1** exhibits the strong and sharp absorption peaks, of 1562 and 1488 cm^{-1} attributed to the v_{as} and v_s vibration of the carboxylate group, respectively, and peaks at 1702 cm^{-1} corresponding to the v(C═O) of carboxylic acid, indicating that the carboxyl groups of H_2bidc ligands are not completely deprotonated. The broad bands at 3155-2500 cm^{-1} indicate the presence of O-H and N-H, and the existence of hydrogen bonding interaction These facts are consistent with the X-ray diffraction results.

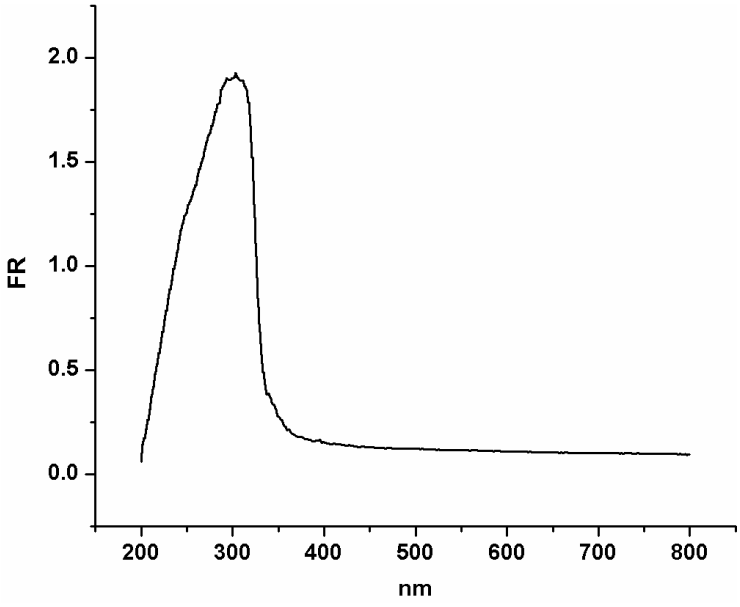


Fig. S11 UV-Visible absorption spectrum of **1**.

In the UV absorption spectra, the strong absorptions at 304 nm for compound **1.** (Fig. S11), is ascribed to the π→π* transitions of ligands.

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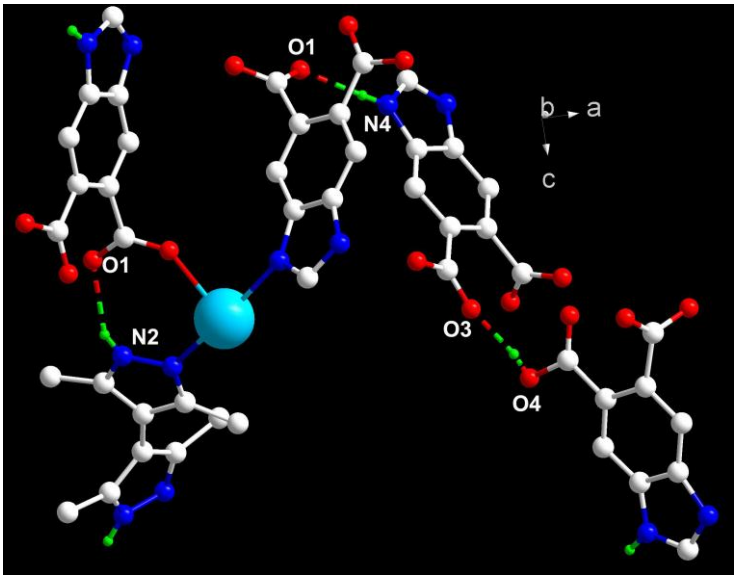

Fig. S12 View of three types of hydrogen bonds.

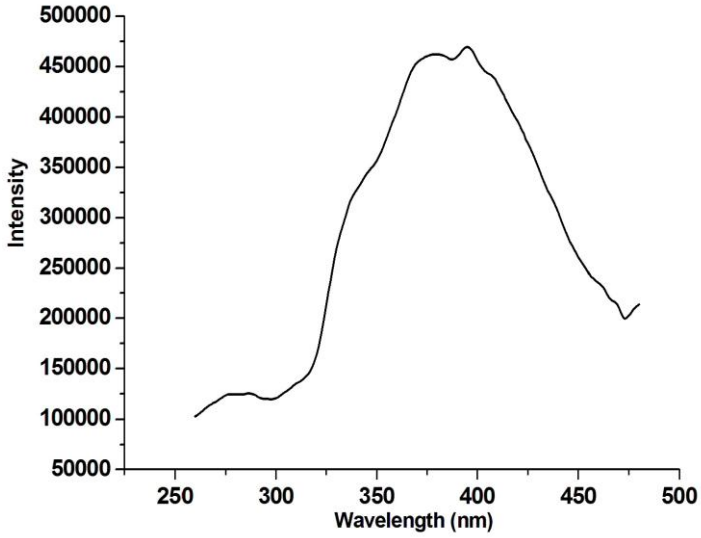

Fig. S13 Excitation spectrum of **1**

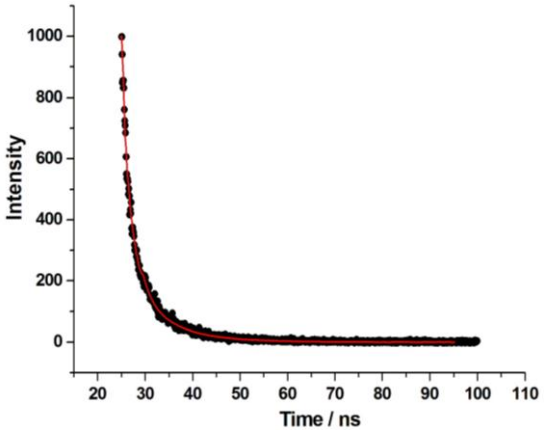

Fig. S14 The lifetime of fluorescence-emission for **1**

Fit Parameters

Fit = A + B1.exp(-t/T1) + B2.exp(-t/T2) + B3.exp(-t/T3)

	Value	Std Dev		Value	Std Dev	Rel %
T1	1.044E-10	2.694E-11	B1	4.289E-1	9.837E-2	10.48
T2	7.826E-9	1.753E-10	B2	2.667E-2	1.338E-3	48.85
T3	1.959E-9	8.201E-11	B3	8.870E-2	2.670E-3	40.67
Chisq	1.379E+0		A	-3.760E-1		

The luminescence decay curves of **1** at room temperature are well fit into a triexponential function as $I = A + B1 \times \exp(-t/\tau_1) + B2 \times \exp(-t/\tau_2) + B3 \times \exp(-t/\tau_3)$. The emission decay lifetimes are τ_1 = 0.10 ns (10.48%), τ_2 = 7.82 ns (48.85%) and τ_3 = 1.96 ns (40.67%) (χ^2 = 1.379) for **1.**