

Assembled bright green fluorescent zinc coordination polymer†

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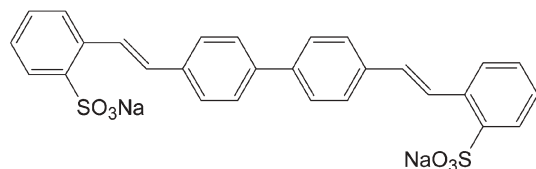
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A 1D zinc coordination polymer with bright green fluorescence, $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})_4][\text{Zn}(4,4'\text{-bipy})_{1.5}(\text{L})(\text{H}_2\text{O})_2]_2(\text{L})\cdot 6\text{H}_2\text{O}$ ($\text{L} = 4,4'\text{-bis}(2\text{-sulfonatostyryl})\text{biphenyl}$), has been designed, hydrothermally synthesized and characterized; the interesting structure consists of three types of infinite chain: a neutral sandwich-like chain, ionic and cationic chains.

Recently numerous coordination polymers consisting of transition-metal ions and bridging organic ligands have been designed and synthesized due to their structural diversities and many intriguing properties such as gas adsorption, enantioselective separation, catalysis, electrical conductivity, non-linear optics, and so on.^{1–8} Particularly, coordination polymers with fluorescent properties are of great interest for their potential applications as light-emitting diodes (LEDs) due to two reasons:^{1,9–37} (i) coordination polymers usually exhibit higher thermal stability and stronger intensity than those of free organic ligands; (ii) the emission wavelength of organic ligands would be affected after coordination by transition-metal ions, such as bathochromic-shift^{10–13} and blue-shift.^{9,13} These luminescent properties may be assigned to ligand-to-metal charge transfer (LMCT),^{9,13–21} metal-to-ligand charge transfer (MLCT),²² intraligand $\pi\text{-}\pi^*$ transition^{10,13,23–27} and metal centered transitions.^{13,28,29} On the other hand, 4,4'-bipyridine (4,4'-bipy) has been extensively used as a bridging ligand to construct nanoporous cationic frameworks^{38–42} as well as a luminescent activator.³² A possible development is a nanoscale fluorescent building block combined with the above mentioned nanoporous cationic frameworks *via* charge compensation along with covalent bonds, hydrogen bonds and $\pi\text{-}\pi^*$ stacking interactions. In this paper, disodium 4,4'-bis(2-sulfonatostyryl)biphenyl (Scheme 1) of



Scheme 1 View of disodium 4,4'-bis(2-sulfonatostyryl)biphenyl.

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† Electronic supplementary information (ESI) available: Fig. S1: XRD patterns of experimental and simulated from single crystal data of **1**. Fig. S2: TGA and DTA curves of **1**. Fig. S3: Polyhedral view of the neutral chain of **1**. Fig. S4: View of the $\pi\text{-}\pi^*$ stacking interactions of the ionic chain of **1**. Fig. S5: Emission spectra excited at 290, 368 and 426 nm of **1**. Fig. S6: Solid-state excitation and emission spectrum for **1**, Na_2L and 4,4'-bipy. Fig. S7: Solid-state excitation and emission spectrum for dehydrated **1**. See <http://dx.doi.org/10.1039/b509695b>.

about 2.0 nm length, which is extensively used as a fluorescent brightener, was assembled with a zinc/4,4'-bipy framework into a novel organic–inorganic hybrid material, $[\text{Zn}(4,4'\text{-bipy})(\text{H}_2\text{O})_4][\text{Zn}(4,4'\text{-bipy})_{1.5}(\text{L})(\text{H}_2\text{O})_2]_2(\text{L})\cdot 6\text{H}_2\text{O}$ (**1**), where L is 4,4'-bis(2-sulfonatostyryl)biphenyl. The new compound emits strong green luminescence under excitation with broad wavelength range (UV or violet). The intriguing structure of **1** consists of a neutral sandwich-like chain, anionic and cationic chains *via* hydrogen bonds and $\pi\text{-}\pi^*$ stacking interactions.

Yellow prism-shaped crystals of **1** were obtained with about 68% yield after a mixture of $\text{Zn}(\text{CH}_3\text{COO})_2\cdot 2\text{H}_2\text{O}$, Na_2L , 4,4'-bipyridine and water in the molar ratio 2:1:2:5560 was held at 110 °C for 96 h. The pH value of the final mixture was 4.96. The powder XRD pattern was in agreement with that simulated from single-crystal X-ray data,[‡] which indicated the homogenous phase purity of the product. Elemental analyses identified the formula. The structure of **1** was also supported by its IR spectrum.[§] The TGA and DTA curves indicate an obvious weight loss stage between 50 and 250 °C centered at 193 °C, possibly corresponding to loss of the water molecules (calc. 9.6%, found 9.2%). Following this, a continuing weight loss stage appeared due to the collapse of the compound.

As shown in Fig. 1, $\text{Zn}^{1\text{II}}$ and $\text{Zn}^{2\text{II}}$ atoms are in slightly distorted $[\text{Zn}1\text{N}_3\text{O}_3]$ and $[\text{Zn}2\text{N}_2\text{O}_4]$ octahedral coordination geometries, respectively. The $\text{Zn}^{1\text{II}}$ atom is surrounded by three N donors from three 4,4'-bipys, one oxygen atom of the coordinated L group, and two aqua ligands. The $\text{Zn}^{2\text{II}}$ atom is coordinated by two 4,4'-bipys and four aqua ligands. The distances of Zn–N and Zn–O are in the ranges 2.118(4)–2.206(4) and 2.099(4)–2.191(4) Å, respectively. Except for the coordinated L group, there is also a free L group which does not take part in coordination with Zn^{II} atom.

The intriguing 1D polymer contains three attractive structural features. First, it contains a $[\text{Zn}(4,4'\text{-bipy})_{1.5}(\text{L})(\text{H}_2\text{O})_2]_n$ neutral chain consisting of $[\text{Zn}(4,4'\text{-bipy})_{1.5}]_n^{2n+}$ ladder-like cationic core sandwiched by the coordinated L groups (Fig. 2). In the neutral chain, four $\text{Zn}^{1\text{II}}$ atoms and four 4,4'-bipys form an almost square framework with 1.1×1.1 nm dimensions (calculated from the distance of neighboring Zn^{II} atoms). The coordinated L group attaches to square framework through a covalent bond (Zn1–O7 2.162(4) Å) with one SO_3 terminal group. However, the other SO_3 terminal group interacts with the square framework not with a covalent bond, but through one strong ($\text{O}3\cdots\text{O}10$ 2.665(6) Å) hydrogen bond. Thus, each side of the framework is partly covered by the organic units of two coordinated L groups. The neutral chains are parallel to the *a* axis resulting in one-dimensional channels along the *b* axis. Secondly, the free L groups are enclosed in the above mentioned 1D channels (Fig. 2). In the channels, the free L groups interact each other through offset face-to-face $\pi\text{-}\pi^*$

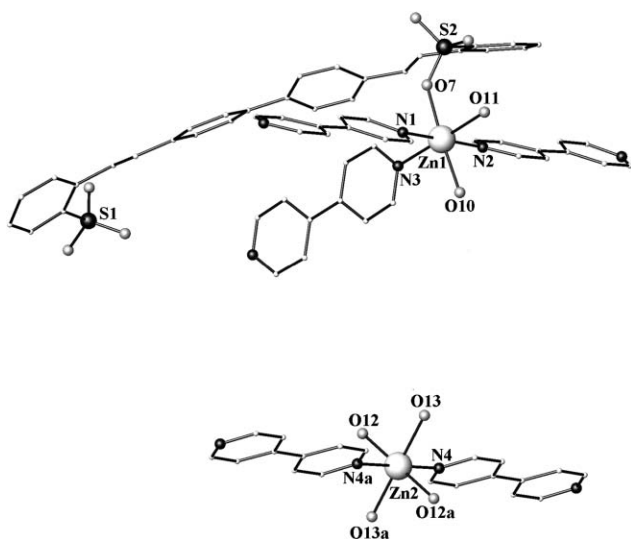


Fig. 1 Ball-and-stick representation of the coordination spheres of Zn^{II} atoms. The hydrogen atoms are omitted for clarity. Symmetry transformations used to generate equivalent atoms: a: $-1 - x, -y, -1 - z$. Selected bond lengths (Å) and angles (°): Zn–N1 2.118(4), Zn1–N2 2.129(4), Zn1–N3 2.206(4), Zn1–O7 2.162(4), Zn1–O10 2.191(4), Zn1–O11 2.142(4), Zn2–N4 2.120(4), Zn2–O12 2.099(4), Zn2–O13 2.161(4); N1–Zn1–N2 177.3(2), N1–Zn1–N3 91.2(2), N1–Zn1–O7 92.1(2), N1–Zn1–O10 88.3(2), N1–Zn1–O11 89.9(2), N2–Zn1–N3 90.6(2), N2–Zn1–O7 90.0(2), N2–Zn1–O10 89.5(2), N2–Zn1–O11 88.4(2), O7–Zn1–O10 176.2(2), O7–Zn1–O11 89.5(2), O10–Zn1–O11 86.8(2), O11–Zn1–N3 178.2(2), O7–Zn1–N3 89.1(2), O10–Zn1–N3 94.7(2), N4–Zn2–O12 90.1(2), N4–Zn2–O13 90.1(2), O12–Zn2–O13 91.0(2).

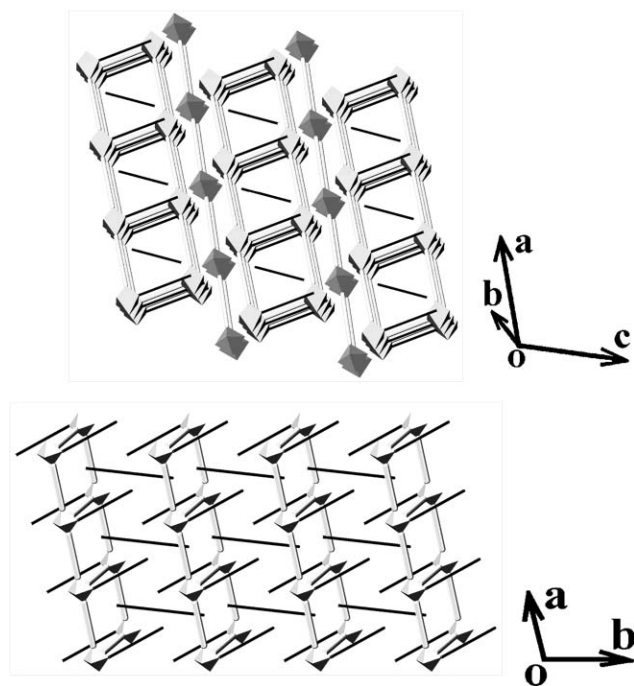


Fig. 2 Packing view of the 1D structure of compound **1**. Gray octahedra: [ZnN₃O₃] or [ZnN₂O₄], White thick line: 4,4'-bipyridine, black thin line: 4,4'-bis(2-sulfonatostyryl)biphenyl.

stacking interactions, with about 3.50 Å separation and about 3.68 Å centroid–centroid distance of terminal benzene rings, into an [L]_n^{2n−} ionic chain. As a result, neutral chains are interpenetrated by the ionic chains into a 2D inorganic–organic hybrid layer. Thirdly, cationic chains ([Zn(4,4'-bipy)(H₂O)₄]_n²ⁿ⁺) are sandwiched by the hybrid layers through two strong (O1⋯O12 2.716(7) Å and O5⋯O13 2.682(6) Å) and one weak (O1⋯O13 3.032(8) Å) hydrogen bond. In addition, the free water molecule (O14) plays an important role in the structure, which links the neutral, ionic and cationic chains with one weak (O8⋯O14 2.927(8) Å), one strong (O5⋯O14 2.681(8) Å) and one strong (O12⋯O14 2.659(7) Å) hydrogen bond, respectively.

Besides the novel structure, as expected, the complex **1** possesses attractive fluorescent properties. Compound **1** emits a very strong green luminescence with peak maximum band at 542 nm, about 39 ns lifetime and 2.8% intensity of Na₂L (Fig. 3), which is quite different from the common blue luminescence for the reported coordination polymers.^{10,12,13,16,18–20,23,26,27,30,31,37} Since zinc/4,4'-bipy complexes display blue luminescence due to the intraligand fluorescent emission of 4,4'-bipys,³⁷ the emission spectrum of **1** probably originates from a ligand-centred π–π* transition of L.^{10,13,23–27} There is an intriguing fluorescent character of solid **1** which exhibits about 90 nm bathochromic-shift compared to that of Na₂L (λ_{max} = 452 nm, excited at 410 nm), resulting in the transformation of luminescent color. To the best of our knowledge, the bathochromic shift of previously reported coordination polymers are all in the blue range with a maximum of 30 nm.^{10,11,13,37} In addition, compound **1** can also emit the same strong green fluorescence when excited at 290 and 368 nm rather than 426 nm, according to the broad excitation spectrum displaying three peaks at 290, 368 and 426 nm. The excitation peaks at 290 and 368 nm are probably attributable to the intraligand π–π* stacking interaction of L and intraligand 4,4'-bipy, respectively. Besides ultraviolet radiation, compound **1** can also be excited with violet light. This behavior is obviously different from that reported for common coordination polymers in previous studies. From the above we can see that solid **1** exhibits another intriguing character, transforming violet light to green fluorescence. The XRD pattern indicates the structure of **1** has been changed after it is dehydrated under N₂ atmosphere at a

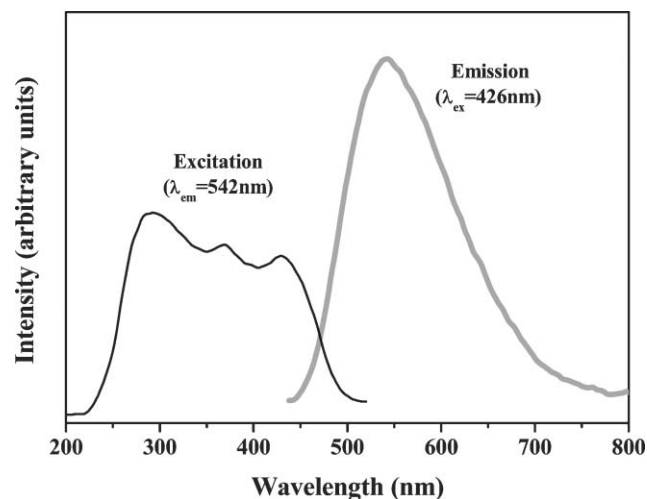


Fig. 3 Solid-state excitation and emission spectrum for **1**.

heating rate of 10 °C min⁻¹ from room temperature to 200 °C. However, the dehydrated solid of **1** also shows a strong green luminescence with a peak maximum band at 543 nm, about 19 ns lifetime and broad excitation spectrum, which are similar to those of solid **1**.

In conclusion, we have successfully designed and synthesized a novel organic-inorganic hybrid compound with fluorescer brightener (disodium 4,4'-bis(2-sulfonatostyryl)biphenyl), 4,4'-bipy and zinc. Compound **1** exhibits novel structure as well as intriguing fluorescent properties, including strong intensity, maximum bathochromic-shift and the transformation of violet light to green fluorescence. The search for other materials with different ratios of reactants and metals (transition metals and rare-earth) is under way.

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Notes and references

‡ Crystal data for C₁₂₄H₁₂₀N₈O₃₂S₆Zn₃ **1**: triclinic, space group *P* $\bar{1}$; 0.28 × 0.15 × 0.08 mm; *a* = 11.3336(15), *b* = 17.332(3), *c* = 17.721(3) Å, α = 110.910(6), β = 99.2770(10), γ = 107.205(3)°, *V* = 2964.3(8) Å³, *Z* = 1; *D*_c = 1.469 g cm⁻³; μ = 0.792 mm⁻¹; λ = 0.71073 Å; *F*(000) = 1362; *T* = 293.15 K; Rigaku Mercury CCD/AFC diffractometer; 837 parameters refined; 18467 reflections were measured in the range of 6.42 ≤ 2θ ≤ 49.42°, 10036 independent reflections (*R*_{int} = 0.0437), 7428 observed reflections [*I* > 2σ(*I*)] with *R*₁ = 0.0791 and *wR*₂ = 0.1509; *R*₁ = 0.1084 and *wR*₂ = 0.1714 (all data). The structure was solved by direct methods and refined by full-matrix least-squares techniques on *F*² using SHELXTL-97.⁴³ All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms attached to carbon atoms were generated geometrically. Idealized positions of H atoms of H₂O molecules were fixed with O–H = 0.96 Å and H···H = 1.52 Å. CCDC 277387. See <http://dx.doi.org/10.1039/b509695b> for crystallographic data in CIF or other electronic format.

§ Elemental analysis (%) calc. for C₁₂₄H₁₂₀N₈O₃₂S₆Zn₃ **1**: C 56.78, H 4.61, N 4.27%. Found: C 56.71, H 4.45, N 4.37%. IR (KBr pellet, cm⁻¹): 3350s (ν_{O-H}), 3060w (ν_{C-H}), 3025w (ν_{C-C-H}), 1612s, 1563w, 1537m, 1495m, 1464m, 1416m, 1213s, 1163s, 1134s, 1082m, 1045w, 1016s, 976w, 812s, 768w, 755w, 729w, 717w, 636w, 615m, 563m, 542m.

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