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# Chemical Communications

## COMMUNICATION

### Encapsulation of the $[\text{Ru}(\text{bpy})_3]^{2+}$ Luminophore in a Unique Hydrogen-Bonded Host Framework

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**The ubiquitous luminophore  $[\text{Ru}(\text{bpy})_3]^{2+}$  can be sequestered as a guest in an unusual guanidinium organosulfonate host framework architecture that guides the  $[\text{Ru}(\text{bpy})_3]^{2+}$  into 1D zigzag chains that suggest unique through-space energy transfer characteristics.**

Crystalline inclusion compounds,<sup>1,2,3,4</sup> which span metallacages,<sup>5,6</sup> metal-organic frameworks,<sup>7,8,9</sup> covalent organic frameworks,<sup>10,11,12</sup> hydrogen-bonded organic frameworks,<sup>13,14</sup> and porous organic cages,<sup>15,16</sup> remain promising candidates as materials for optoelectronics, magnetics, storage of sensitive compounds and chemical reactions under confinement. Their unique potential stems from the versatility of organic synthesis and the ability to design function on demand.

Our laboratory has reported a series of crystalline inclusion compounds based on two-dimensional hydrogen-bonded sheets of complementary guanidinium (G) ions and organosulfonate (S) ions assembled through charge-assisted N-H...O-S hydrogen bonds. The threefold symmetry, combined with the hydrogen bond complementarity and opposite charges of the ions, afford a persistent charge-assisted "quasi-hexagonal" hydrogen-bonding network equipped with inclusion cavities in crystalline layered,<sup>17,18</sup> cylindrical<sup>19,20</sup> and even cubic<sup>21</sup> frameworks. The size and character of the cavities can be modified through judicious selection of organosulfonate moieties without altering the hydrogen-bond connectivity of the GS sheets.<sup>22,23,24,25</sup> These frameworks have illustrated the principle of separating function (provided by the guests) from structure (provided by the framework), which promises to simplify crystal engineering strategies for functional materials.<sup>26</sup> In particular, these frameworks are capable of including organic dyes as guests, such as pyrene, perylene and coumarin and its derivatives, with control of the aggregation state (i.e. monomers vs. dimers, H- vs J-aggregates) achieved by proper design of the organodisulfonate pillar in the GS framework.<sup>27,28</sup> Consequently,

the fluorescence emission characteristics can differ substantially from those observed for dye monomers in solution.

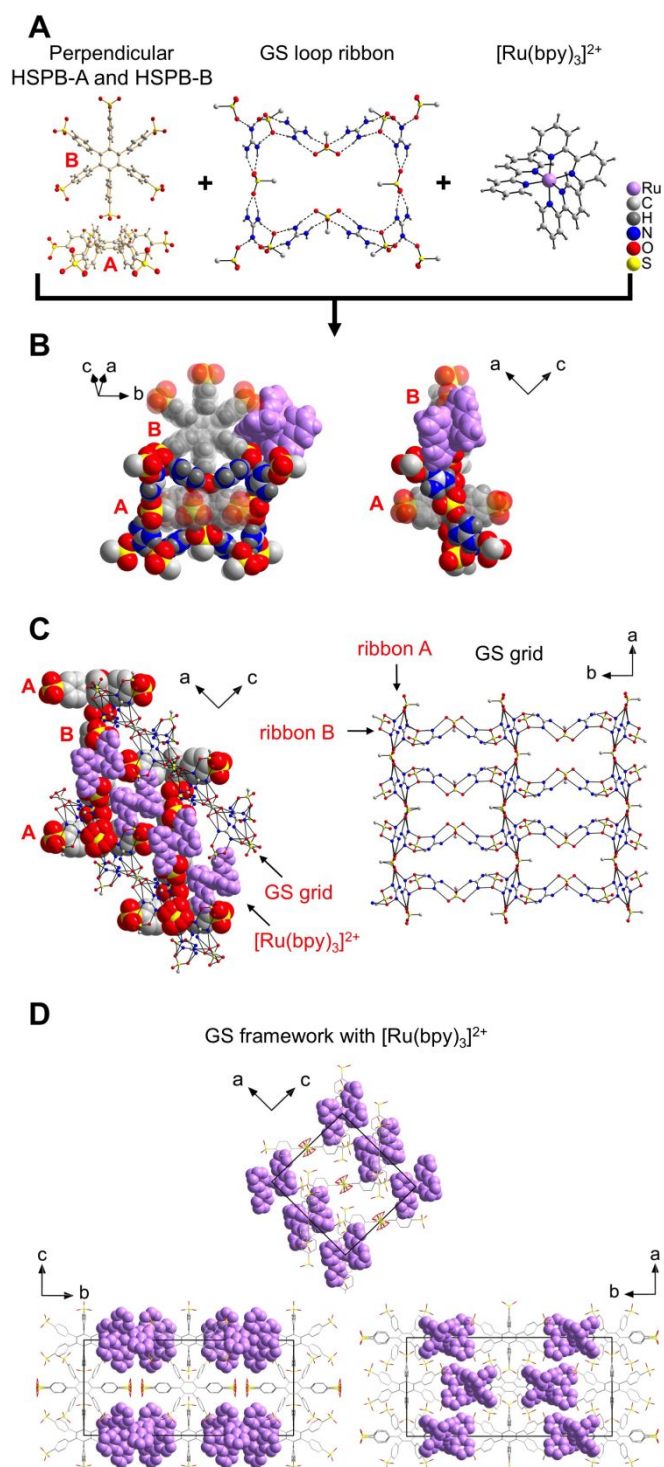
The ubiquitous cation  $[\text{Ru}(\text{bpy})_3]^{2+}$ , a well-known photosensitizer, enables various organic transformations that cannot be achieved thermally or photochemically,<sup>29</sup> and it has been used widely as a sensitizer for light-driven water oxidation,<sup>30,31</sup> photochemical hydrogen production,<sup>32,33,34</sup> and solar energy devices.<sup>35</sup> These unique properties have prompted investigations of  $[\text{Ru}(\text{bpy})_3]^{2+}$  as guests in polymeric and metal-organic frameworks, with effective solid-state concentrations as high as 1.5 M.<sup>36</sup> Herein we report a new inclusion compound with a high concentration of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions encapsulated within an unusual GS hydrogen-bonded framework that enforces 1D zigzag chains of  $[\text{Ru}(\text{bpy})_3]^{2+}$  that may be an interesting candidate for investigations of through-space energy transfer.

The hydrogen-bonded inclusion compound with the simplified formula  $\text{G}_4\text{HSPB}\cdot[\text{Ru}(\text{bpy})_3]^{2+}$  (**1**) was obtained as millimeter-sized, block-shaped, red crystals by slow evaporation from dimethylformamide (DMF):water:formic acid solutions containing hexa(4-sulfonatophenyl)benzene (HSPB<sup>6-</sup>) (Fig. 1A), guanidinium chloride and  $[\text{Ru}(\text{bpy})_3]^{2+}$  (see Supporting Information for synthetic details). Compound **1** crystallizes in the centrosymmetric space group  $C2/m$  with 4 formula units per unit cell ( $a=16.88 \text{ \AA}$ ,  $b=35.02 \text{ \AA}$ ,  $c=15.96 \text{ \AA}$ ,  $\beta=91.02^\circ$ ,  $V=9433 \text{ \AA}^3$ ). The asymmetric unit contains one-quarter each of two crystallographically independent HSPB<sup>6-</sup> anions, two guanidinium ions, one-half of a  $[\text{Ru}(\text{bpy})_3]^{2+}$  guest, and solvent molecules (0.5 water, 0.5 DMF). No other solvent molecules or species could be identified in the difference Fourier map and their contributions were treated using the SQUEEZE routine of the program PLATON.<sup>37</sup> The total free volume of the framework is  $1720 \text{ \AA}^3$  (18.2 %) if all solvent is removed, and  $4333 \text{ \AA}^3$  (45.9 %) if the solvent and  $[\text{Ru}(\text{bpy})_3]^{2+}$  guests are removed, as measured by Connolly surfaces with a probe atom having a diameter of  $1.2 \text{ \AA}$  and a grid spacing of  $0.2 \text{ \AA}$ . <sup>1</sup>H NMR analysis of dissolved crystals, however, revealed the presence of dimethylammonium ions and formic acid, as well as DMF, consistent with the actual formula  $\text{G}_4(\text{HSPB})^{6-}[\text{Ru}(\text{bpy})_3]^{2+}(\text{DMF})_2(\text{HCO}_2\text{H})_{1.4}(\text{HCO}_2^-)_{0.6}(\text{H}_2\text{O})(\text{DMA})^{+0.6}$ . The

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formate ion is included here for charge balance, although the presence of some amount of chloride ion (from the guanidinium chloride starting material) cannot be excluded. The unit cell contains four  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions, corresponding to an effective dye concentration in the crystal ( $C_{\text{eff}}$ ) of 0.70 M.

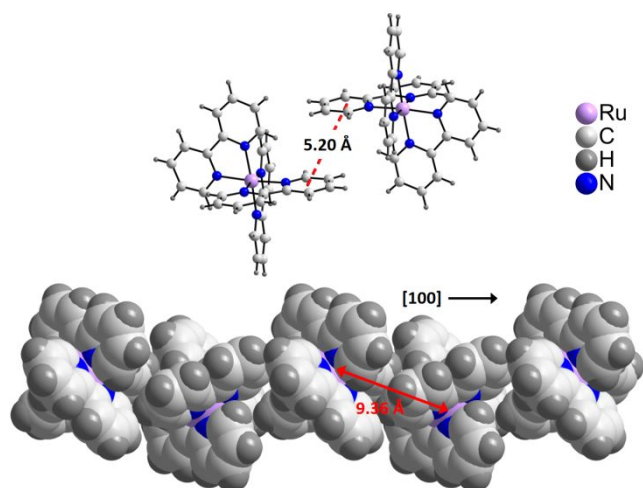


**Fig. 1.** (A) Perpendicular arrangement of HSPB-A and HSPB-B, GS loop ribbon and  $[\text{Ru}(\text{bpy})_3]^{2+}$  guest. (B) View along various orientations of the structural motif within the framework. (C) (left) View along [010] direction of the GS framework reveals  $[\text{Ru}(\text{bpy})_3]^{2+}$  organization along [100] direction and between the GS grids; (right) GS grid. (D) View of

the framework with  $[\text{Ru}(\text{bpy})_3]^{2+}$  guests normal to the (010), (100) and (001) planes (guanidinium ions and solvent molecules are omitted for clarity).

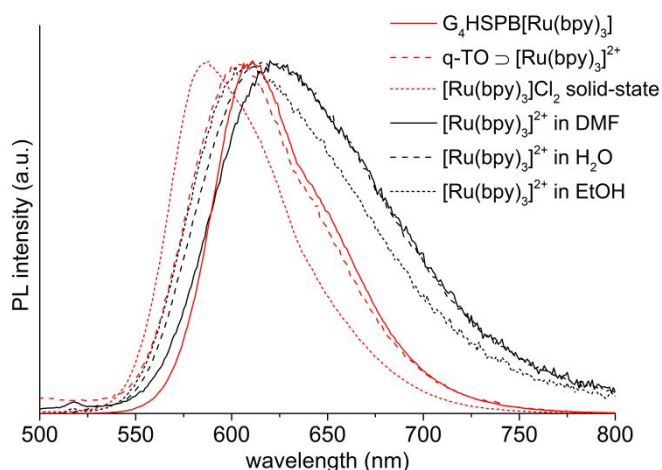
The two crystallographically unique HSPB molecules, denoted HSPB-A and HSPB-B, are mutually perpendicular, wherein a sulfonate group of one is directed toward the central phenyl ring of the other (Fig. 1A). Unlike previously reported GS frameworks,<sup>19</sup> this new framework can be described as having a hydrogen-bonded GS ribbon that forms an unusual loop structure with eight guanidinium ions and eight sulfonate groups (Fig. 1A), with O...N hydrogen bond distances ranging from 2.78 Å - 3.04 Å. The GS loop winds around HSPB-A and a  $[\text{Ru}(\text{bpy})_3]^{2+}$  ion, the latter nestled between two sulfonatophenyl groups of HSPB-B (Fig 1B). The GS loops are interconnected, generating a GS grid in the (001) plane that contains two unique GS ribbons traversing the crystallographic *a* and *b* directions (Fig 1C). Ribbon A contains only sulfonate groups of HSPB-A, and ribbon B contains only sulfonate groups of HSPB-B, the ribbons connected through a disordered guanidinium ion. The ribbons intersect on crystallographic inversion center, consistent with this disordered guanidinium ion serving as a four-fold nodal point. The two-dimensional GS grid can be described with the point symbol  $\{4^4.6^2\}$  and the topology type **sql**.<sup>38</sup> Perpendicular stacking of HSPB-A and HSPB-B anions produces chains along the [101] direction within the framework (Fig 1C). HSPB-A is located within the GS grid because the GS loop ribbon winds around it, whereas HSPB-B serves as a pillar that connects the GS grids in the framework.

The unusual framework in **1** enforces an arrangement of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions that differs from  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions in crystalline  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  ( $d_{\pi-\pi} = 4.68$  Å;  $d_{\text{Ru}-\text{Ru}} = 7.59$  Å)<sup>39</sup> and  $[\text{Ru}(\text{bpy})_3](\text{ClO}_4)_2$  ( $d_{\pi-\pi} = 4.72$  Å;  $d_{\text{Ru}-\text{Ru}} = 8.41$  Å),<sup>40</sup> as well as  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions caged in other frameworks. The  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions, situated between the GS grids, form zigzag chains along the [100] direction (Fig. 1C,D). The ring center-to-ring center distance between pyridine rings of nearest-neighbor  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions along [100] is 5.20 Å. The interplanar separation between these rings is 3.53 Å, but they are offset with negligible  $\pi-\pi$  overlap (Fig. 2). The nearest-neighbor Ru...Ru distance along the [100] chains is  $d_{\text{Ru}\dots\text{Ru}} = 9.36$  Å. The next-nearest neighbor distance is between adjacent chains,  $d_{\text{Ru}\dots\text{Ru}} = 13.46$  Å. The nearest-neighbor  $d_{\text{Ru}\dots\text{Ru}}$  value is, coincidentally, identical to  $d_{\text{Ru}\dots\text{Ru}}$  between  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions metal oxalate-bridged networks<sup>41,42</sup> as well as those confined in non-porous metal oxalate  $\text{Zn}_2(\text{C}_2\text{O}_4)_3$  and  $\text{NaAl}(\text{C}_2\text{O}_4)_3$  frameworks.<sup>43,44</sup> The  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions in the latter frameworks are arranged in a 3D network that supports high energy Ru emission with resolved vibronic structure, attributed to the shielding of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  luminophores from solvent. Moreover, the rates of long-range (through-space) energy transfer between metal centers are greater than reported for through-bond energy transfer in 1D networks of a MOF formed between zinc ions and  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions equipped with carboxylate groups (“ $\text{L}_{\text{Ru}}\text{Zn}$  MOF”).<sup>45</sup> Compound **1**, therefore, represents a unique and interesting candidate for investigating through-space energy transfer in a 1D network.



**Fig. 2** (top) Two nearest-neighbor  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions along the  $[100]$  exhibit a ring center-to-ring center distance of 5.20 Å. The interplanar separation is 3.53 Å, but the pyridine rings are substantially offset such that  $\pi$ - $\pi$  overlap is negligible. (bottom) The zigzag chain of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions oriented along  $[100]$ , with a Ru-Ru nearest neighbor distance of 9.36 Å.

The emission properties of compound **1** crystals, which contain DMF, formic acid, water and dimethylammonium ions, were compared with  $[\text{Ru}(\text{bpy})_3]^{2+}$  in various solvents, including DMF and water (Fig. 3; Table 1). The emission spectrum of **1** exhibited a  $\lambda_{\text{max}} = 611$  nm, corresponding to a small hypsochromic shift compared to  $[\text{Ru}(\text{bpy})_3]^{2+}$  in water ( $\lambda_{\text{max}} = 617$  nm) and DMF ( $\lambda_{\text{max}} = 620$  nm). The  $\lambda_{\text{max}}$  for **1** exhibited a bathochromic shift compared with the  $\lambda_{\text{max}}$  values for  $[\text{Ru}(\text{bpy})_3]^{2+}$  encapsulated in the supramolecular cages of a crystalline zeolite-like hydrogen-bonded framework ( $q\text{-TO}\supset[\text{Ru}(\text{bpy})_3]^{2+}$ ),<sup>46</sup> the aforementioned  $[\text{Zn}_2(\text{oxalate})_3]$ - $[\text{Ru}(\text{bpy})_3]$  and the Zn-based MOF USF2,<sup>47</sup> but comparable to that of the  $\text{L}_{\text{Ru}}\text{Zn}$  MOF. In contrast, **1** exhibited a large bathochromic shift compared with  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  in the solid-state ( $\lambda_{\text{max}} = 588$  nm).



**Fig. 3** Photoluminescence (PL) spectra of compound **1**, compared with  $[\text{Ru}(\text{bpy})_3]^{2+}$  in DMF,  $\text{H}_2\text{O}$  and EtOH, as well as  $q\text{-TO}\supset[\text{Ru}(\text{bpy})_3]^{2+}$  and  $[\text{Ru}(\text{bpy})_3]^{2+}$  in the solid state (chloride salt). Intensities are normalized to the same maximum.

**Table 1.** Emission data for compound **1**,  $[\text{Ru}(\text{bpy})_3]^{2+}$  in various solvents, and  $[\text{Ru}(\text{bpy})_3]^{2+}$  in various solid state compounds.

Compound	Emission ( $\lambda_{\text{max}}$ ) <sup>a</sup>
$\text{G}_4\text{HSPB}\cdot[\text{Ru}(\text{bpy})_3]$ solid-state	611 nm
$[\text{Ru}(\text{bpy})_3]^{2+}$ in DMF	620 nm
$[\text{Ru}(\text{bpy})_3]^{2+}$ in $\text{H}_2\text{O}$	617 nm
$[\text{Ru}(\text{bpy})_3]^{2+}$ in EtOH	611 nm
$q\text{-TO}\supset[\text{Ru}(\text{bpy})_3]^{2+}$ solid-state	604 nm
$[\text{Ru}(\text{bpy})_3]\text{Cl}_2$ solid-state	588 nm
$[\text{Ru}(\text{bpy})_3]^{2+}$ in USF2 MOF	593 nm
$\text{L}_{\text{Ru}}\text{Zn}$ MOF	620 nm
$[\text{Zn}_2(\text{oxalate})_3]$ - $[\text{Ru}(\text{bpy})_3]$	570 (610) nm <sup>b</sup>

<sup>a</sup> $\lambda_{\text{exc}} = 450$  nm. <sup>b</sup>Two peaks observed in the emission spectrum.

In conclusion, the luminophore  $[\text{Ru}(\text{bpy})_3]^{2+}$  has been encapsulated in a crystalline host framework consisting of guanidinium and polyorganosulfonate ions, exhibiting an architecture previously unobserved for this class of hydrogen-bonded frameworks. The caged  $[\text{Ru}(\text{bpy})_3]^{2+}$  exhibits luminescence that reflects the environment of accompanying included solvent and the encapsulating framework, quite distinct from its luminescence in solid  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  but not unlike behavior observed for  $[\text{Ru}(\text{bpy})_3]^{2+}$  trapped in cages of polymeric and metal-organic frameworks. The unique arrangement of the  $[\text{Ru}(\text{bpy})_3]^{2+}$  suggests compound **1** would be an interesting case study for through-space energy transfer in a 1D network.

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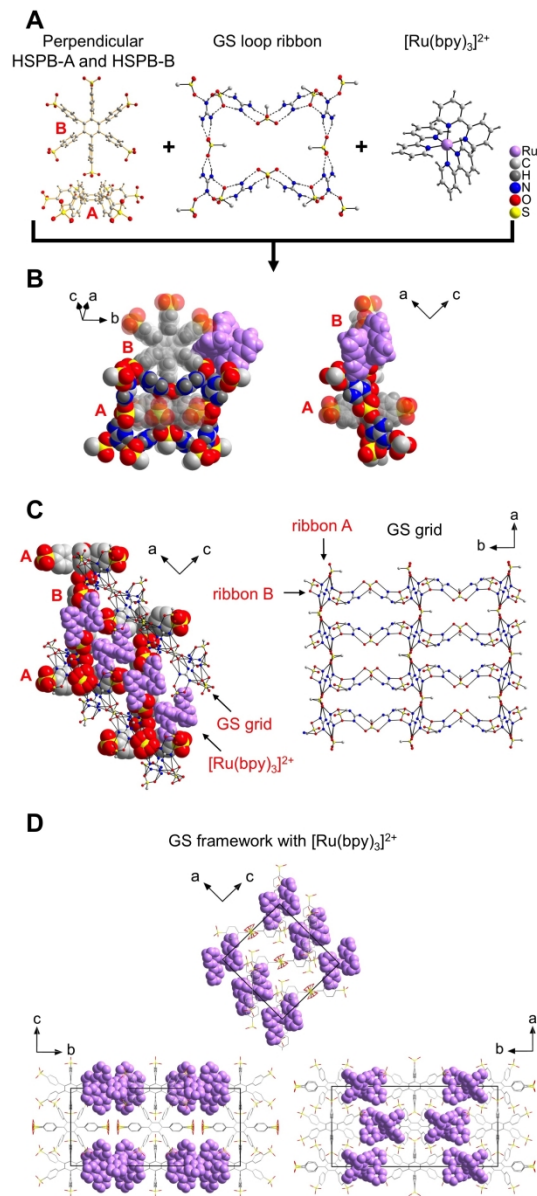


Fig. 1. (A) Perpendicular arrangement of HSPB-A and HSPB-B, GS loop ribbon and  $[\text{Ru}(\text{bpy})_3]^{2+}$  guest. (B) View along various orientations of the structural motif within the framework. (C) (left) View along  $[010]$  direction of the GS framework reveals  $[\text{Ru}(\text{bpy})_3]^{2+}$  organization along  $[100]$  direction and between the GS grids; (right) GS grid. (D) View of the framework with  $[\text{Ru}(\text{bpy})_3]^{2+}$  guests normal to the  $(010)$ ,  $(100)$  and  $(001)$  planes (guanidinium ions and solvent molecules are omitted for clarity).

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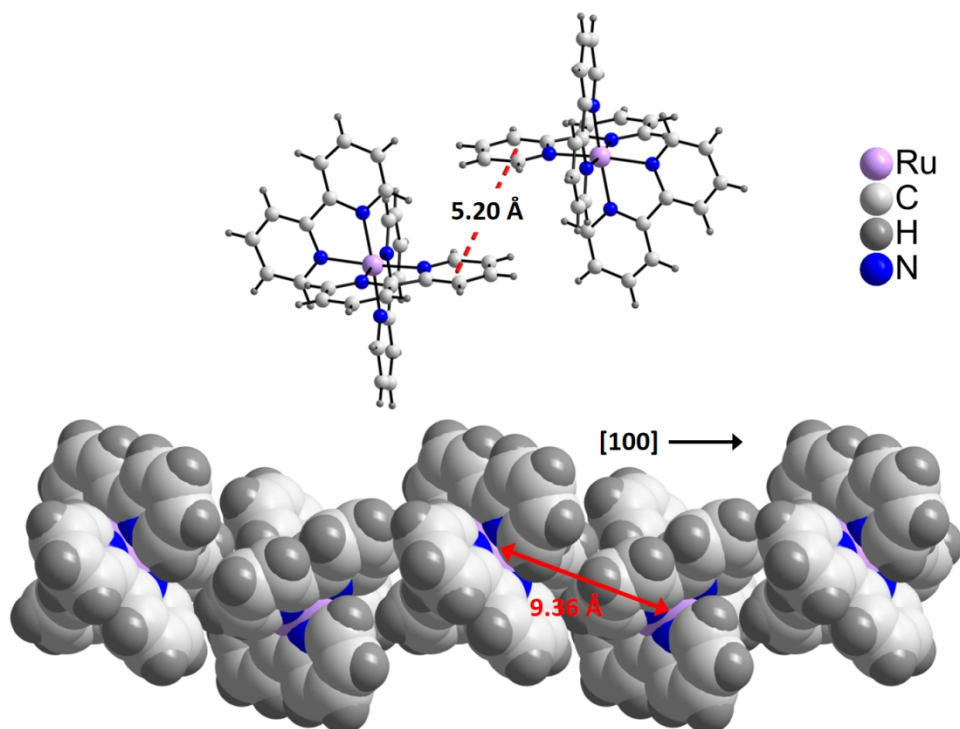


Fig. 2 (top) Two nearest-neighbor  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions along the  $[100]$  exhibit a ring center-to-ring center distance of 5.20 Å. The interplanar separation is 3.53 Å, but the pyridine rings are substantially offset such that n–n overlap is negligible. (bottom) The zigzag chain of  $[\text{Ru}(\text{bpy})_3]^{2+}$  ions oriented along  $[100]$ , with a Ru...Ru nearest neighbor distance of 9.36 Å.

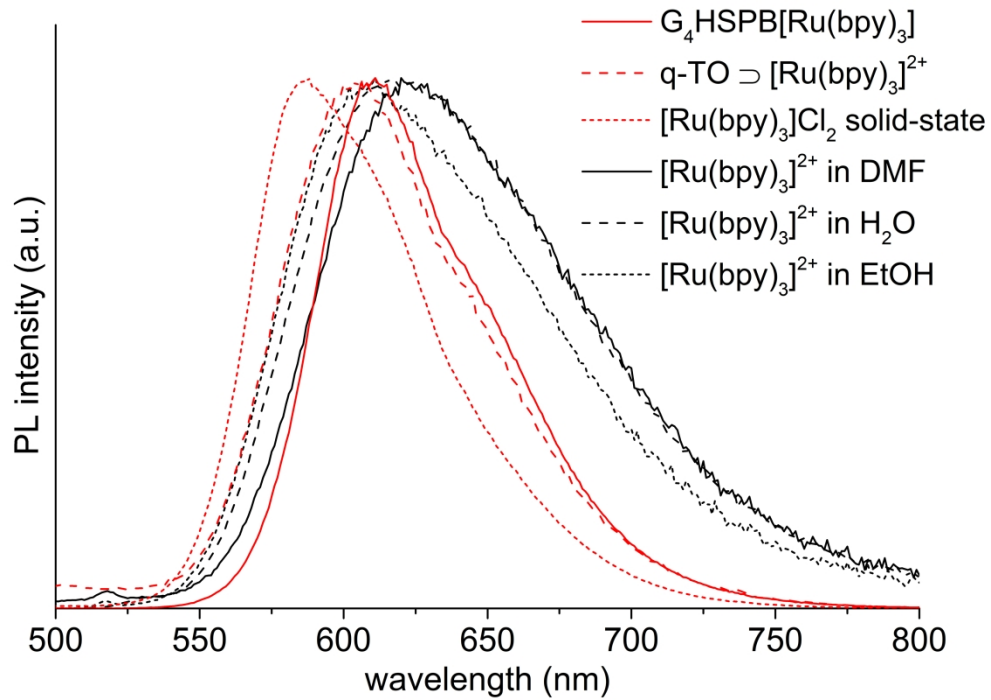
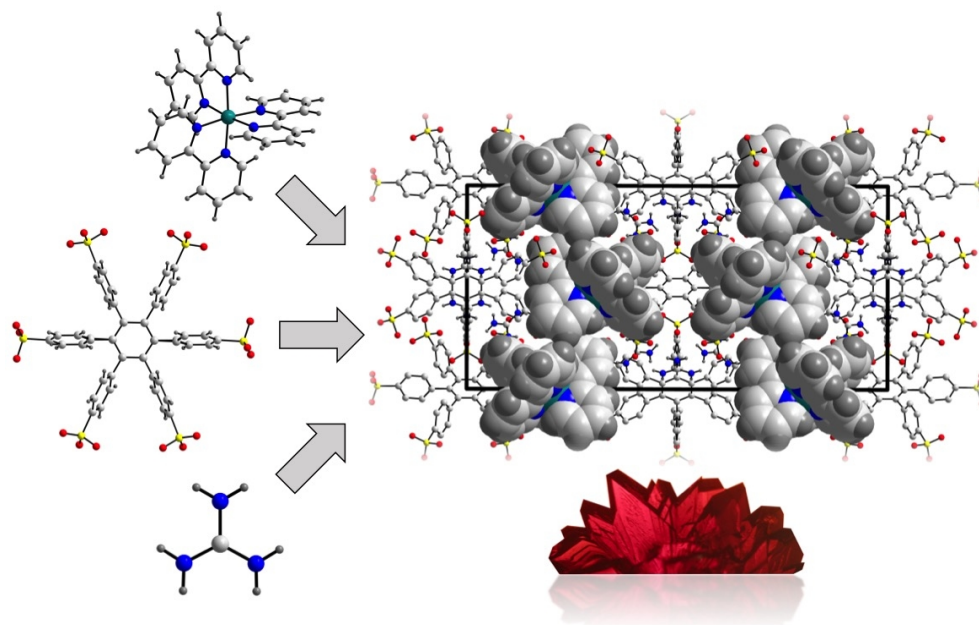


Fig. 3 Photoluminescence (PL) spectra of compound 1, compared with [Ru(bipy)<sub>3</sub>]<sup>2+</sup> in DMF, H<sub>2</sub>O and EtOH, as well as q-TO<sup>+</sup>[Ru(bipy)<sub>3</sub>]<sup>2+</sup> and [Ru(bipy)<sub>3</sub>]<sup>2+</sup> in the solid state (chloride salt). Intensities are normalized to the same maximum.

296x209mm (300 x 300 DPI)



One-dimensional networks of the well-known photosensitizer  $[\text{Ru}(\text{bpy})_3]^{2+}$  are encapsulated in an unusual hydrogen-bonded crystalline host framework.



417x285mm (72 x 72 DPI)