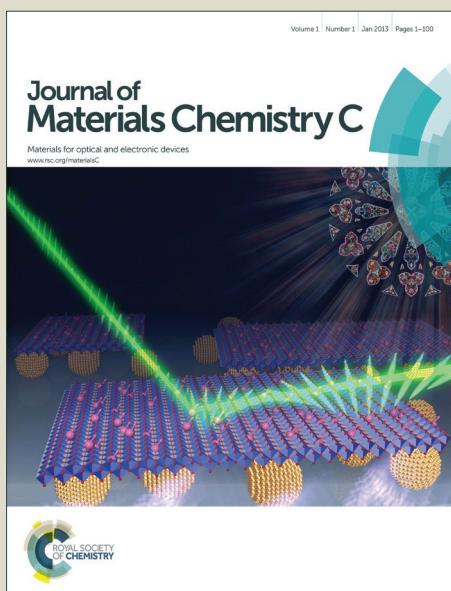


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## Tuning Efficiency of Multi-Step Energy Transfer in Host-Guest Antennae System based on Chalcogenide Semiconductor Zeolite through Acidification and Solvation of Guests<sup>†</sup>

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We reported a new case of multi-step energy transfer process in host-guest antennae system based on chalcogenide semiconductor zeolite (coded as RWY). The multi-step vectorial energy transfer assay was fabricated by encapsulating both proflavine ion (PFH<sup>+</sup>) and pyronine ions (Py<sup>+</sup>) into the RWY porous framework, serving as UV-vis light-harvesting host. The ultraviolet high-energy excitations absorbed by RWY host were channeled to PFH<sup>+</sup> ions and then onto Py<sup>+</sup> ions to give rise of visible-light emission. The steady-state fluorescence and fluorescent dynamics of emission revealed successfully the process of multi-step vectorial energy transfer occurring in RWY⊃(PFH<sup>+</sup>&Py<sup>+</sup>) host-guest antennae system. Moreover, the post treatment of guest ions, such as further acidification of PFH<sup>+</sup> ion and solvation of guest, was also investigated to tune energy transfer efficiency in such host-guest antennae system. The current study shows that deep protonation of PFH<sup>+</sup> as well as solvation of guest ion can dramatically enhance energy transfer efficiency between RWY host and PFH<sup>+</sup>, and even between PFH<sup>+</sup> and Py<sup>+</sup>, much higher than that in untreated host-guest antennae system.

### Introduction

Solar irradiation, as one of clean and sustainable energy, is the focus of attention for scientists and governments since mankind is currently facing the worldwide energy crisis.<sup>1,2</sup> To settle this issue, some artificial systems capable of making fully and efficiently use of solar energy have been developed to extend their broad applications in the field of photo-induced syntheses and photo-driven devices.<sup>3,4</sup> The high-efficiency light-harvesting antennae in those artificial systems, especially simulated photosynthesis systems, is regarded as essence in optimizing solar energy utilization. During the last decade, various intelligently designed artificial photosynthesis-related antennae systems have been created in the goal of maximizing utilization efficiency of solar energy.<sup>1,5,6</sup> Among them, host-guest antennae system represents a promising approach in high-efficiency utilization of solar energy.<sup>7-10</sup> This is because the alignments of guest chromophores as light-absorbing units could be readily

accomplished through induction of host-guest interaction and space confinement effect in host matrix, in which the increased absorption cross-section greatly enhances the photon capture.<sup>11-13</sup>

Oxide-based zeolites, being a class of porous crystalline materials with highly ordered channels, have been widely utilized as host matrix materials in the study of artificial antennae systems for light harvesting and transduction.<sup>14-21</sup> Due to insulating nature of oxide-based zeolites making them intrinsically lacking either the UV- or visible-light absorption or fluorescent property to be involved in a cooperative absorption-transduction energy cascade, some continuous processes (such as energy absorption, migration and transfer) in the host-guest antennae systems mainly occur in the adjacent guest chromophores without host involved. Considering that the host-involved energy transfer system can facilitate the enhancement of energy transfer efficiency through increasing contact areas and shortening distance between donor and acceptor, we recently purposefully created such desired case by replacing oxide-based zeolite with chalcogenide-based zeolite (herein named RWY)<sup>22</sup> as host material, and successfully realized multi-step energy transfer process.<sup>23</sup> This optical active chalcogenide-based zeolite, capable of integrating porosity with semi-conductivity and photoluminescence, provides a whole new opportunity for framework-involved energy transfer between inorganic host and organic guest. Nevertheless, in this case, the energy transfer efficiency (12%) between RWY host and guest dye molecule did not reach our expectation. Thus, we are still confronted with a big

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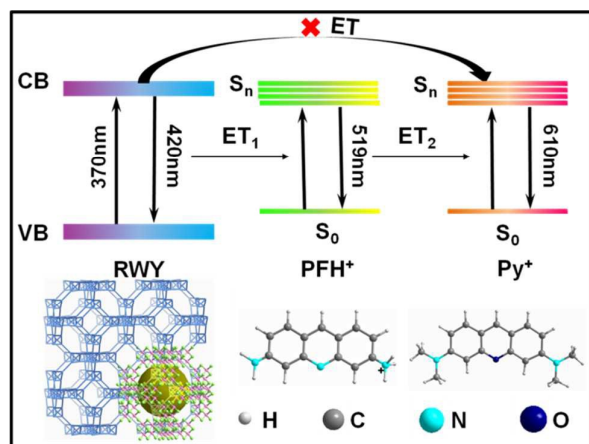
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challenge on how to boost multi-step energy transfer efficiency in such host-guest antenna system.

It is generally accepted that energy transfer efficiency is controlled by three parameters: spectral overlap degree between donor emission spectrum and acceptor absorption spectrum, the relative orientation of transition dipoles in donor-acceptor pair, and the distance of donor and acceptor molecules.<sup>14</sup> Any adjustment altering above three parameters can tune energy transfer efficiency. The type of guest molecules or ions in host-guest antennae system as well as their solvation can potentially alter the spectral overlap, the dipoles and even distance between donor and acceptor.<sup>3,8</sup> Therefore, the in-situ post treatment of guest molecules or ions in host matrix could be very interest and effective method to tune energy transfer efficiency.

Upon above consideration, in this work, we firstly encapsulated both proflavine ion (PFH<sup>+</sup>) and pyronine ions (Py<sup>+</sup>) as guests into the pore space of RWY host framework, and successfully realized the multi-step energy transfer process in such host-guest antennae system, in which the ultraviolet high-energy excitations absorbed by RWY host were channeled to PFH<sup>+</sup> ions and then onto Py<sup>+</sup> ions to give rise of visible-light emission (Scheme 1). Most importantly, the acidification of guest PFH<sup>+</sup> dramatically enhanced energy transfer efficiency from 14% to 33.7% and 29.1% to 37.8% for RWY-PFH<sup>+</sup> and PFH<sup>+</sup>-Py<sup>+</sup> donor-acceptor pairs, respectively. In addition, solvation of guest ions (PFH<sup>+</sup> and Py<sup>+</sup>) also exhibited its capability in tuning energy transfer efficiency in the host-guest antenna system. To the best of our knowledge, investigation on tuning energy transfer efficiency though in-situ post treatment of guests in host-guest antennae system has never been carried out before this work, and current method can be also adopted to explore the energy transfer process in other chalcogenide-based host-guest system.<sup>24-26</sup>

**Scheme 1 Multi-step energy transfer processes in RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest antennae system.**



## Experimental Section

### Materials

Sulfur (S, > 99%, powder), germanium oxide (GeO<sub>2</sub>, HP, powder), gallium metal (Ga, AP, bulk), cesium chloride (CsCl, 99%, solid), tris(2-aminoethyl)amine (TAEA, 96%, liquid), proflavine hemisulfate ((PFH<sup>+</sup>)<sub>2</sub>·SO<sub>4</sub><sup>2-</sup>, 98%, powder), pyronine (Py<sup>+</sup>·Cl<sup>-</sup>, > 55%, powder) and vitriol (≥ 70%, liquid) were all used as received without any further purification.

### Synthesis of chalcogenide-based zeolite RWY $\supset$ TAEA (host)

Zeolite material RWY was synthesized according to literature method with minor modification.<sup>22</sup> Small pieces of Ga metal (1.19 mmol, 82.7 mg), GeO<sub>2</sub> (1.04 mmol, 109.1 mg), S powder (6.93 mmol, 222.1 mg), and 2.1719 g of TAEA were mixed in a 23mL Teflon-lined vessel under room temperature with the vigorous stirring for about half an hour, and an opaque brown suspension was formed, then the suspension was sealed in the autoclave and heated at 190°C for 6 days. When the autoclave was cooled to room temperature, pale yellow crystals were obtained together with amorphous powder and a small amount of gallium metal. The mixture products were then ultra-sonicated and washed with ethanol (95%) to float away small particles of amorphous powder and gallium, dodecahedral crystals were recovered with a yield of ~67% according to gallium amount.

### Removal of protonated TAEA templates for pore opening

40 mg of RWY $\supset$ HTAEA<sup>+</sup> crystals were dispersed in 10 mL CsCl solution (1 mol/L) under 85°C for twice to completely remove template ions in the pore space of RWY through ion exchange. Crystals of RWY $\supset$ Cs<sup>+</sup> were finally collected by suction filtration and vacuum dried under room temperature.

### Preparation of PFH<sup>+</sup> or/and Py<sup>+</sup> loaded host-guest antennae system

Encapsulation of dye ions into RWY framework was realized via ion exchange methodology. 40 mg of RWY $\supset$ Cs<sup>+</sup> crystals were firstly placed into 5 mL PFH<sup>+</sup> solution (10<sup>-5</sup> mol/L) for two days under room temperature. RWY $\supset$ Cs<sup>+</sup> crystals distinctly varied their color from pale yellow to bright yellow, and simultaneously the yellow solution faded away, which indicated PFH<sup>+</sup> ions were entrapped into the pore space of RWY to form RWY $\supset$ PFH<sup>+</sup> host-guest system. The driving force of dyes entering into pores is attraction between negatively-charged RWY framework and positively-charged dye molecules. The resulting solid sample was washed with ethanol and water for several times to remove the redundant surface-adsorbed PFH<sup>+</sup> ions. RWY $\supset$ Py<sup>+</sup> host-guest composite was obtained through similar method with that of RWY $\supset$ PFH<sup>+</sup>. To obtain dual-dyes-encapsulated RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest composites, the RWY host material (40 mg) was directly immersed in the mixed solution (5mL) of PFH<sup>+</sup> (10<sup>-5</sup> mol/L) and Py<sup>+</sup> (10<sup>-5</sup> mol/L) for two days under room temperature. UV-vis absorption spectral measurement on above ion-exchanged mother solution indicated that almost all of PFH<sup>+</sup> and Py<sup>+</sup> ions were entrapped into the host framework. All of above host-guest composites were filtrated and vacuum dried under room temperature for subsequent spectral testing. In addition, to prepare acidified RWY $\supset$ PFH<sup>+</sup> or RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest composites, 5mL of PFH<sup>+</sup> (10<sup>-5</sup> mol/L) solution was in advance acidified by adding different amount (20  $\mu$ L, 40  $\mu$ L) of H<sub>2</sub>SO<sub>4</sub> (18mol/L) before ion exchange.

### Solvent treatment of RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest composite

The dye-encased RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) crystalline samples were firstly vacuum degased at 100°C to remove water molecules entrapped in the pores, then was placed in glass vessel filled with the organic solvent vapor (ethanol, THF, DMF, dichloromethane and toluene, respectively) for one day. The solvent-treated samples were quickly collected for subsequent spectral testing.

### Characterizations

The as-synthesized and dye-encased RWY crystalline samples were characterized by power X-ray diffraction that were collected on a desktop diffractometer (D2 PHASER, Bruker, Germany) using Cu-

K $\alpha$  radiation operated at 30 kV and 10 mA. Elemental analysis of C, H, N was performed by VARIDEL III Elemental analyzer. Nitrogen adsorption-desorption isotherms were measured on Micromeritics ASAP 2020 HD88. The distribution of chromophores was characterized by Confocal Laser Scanning Microscope (CLSM) with a 405 nm excitation laser source. Absorption spectra of dye and dye-loaded RWY host-guest composites were recorded with SHIMADZU UV-3600 UV-vis Spectrograph. Fluorescence spectra of the host-guest antenna system were measured at 25°C using a Fluorolog-3 spectrofluorometers with a 450 W Xe lamps as light source. Time-resolved fluorescence behaviors were measured via time-correlated single-photon counting (TCSPC) technique. The energy transfer efficiency is calculated according to equation of  $\eta_{ET} = 1 - \tau_{DA}/\tau_D$ .<sup>27</sup>

## Results and Discussion

### Fabrication and characterization of zeolite antennae system

RWY host, dye entrapped RWY $\supset$ PFH<sup>+</sup>, RWY $\supset$ Py<sup>+</sup> and RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest composites were synthesized as described in experimental section. The powder X-ray diffraction pattern (PXRD) of these prepared materials displayed sharp peaks (Figure S1), which indicated that the post-treatment of ion exchange and subsequent acidification did not destroy the crystallinity of original host framework. N<sub>2</sub> sorption isotherms at 77 K displayed a typical type-I adsorption-desorption behavior, which reveals the typical microporous nature of unloaded and dye-loaded RWY framework (Figure S2-S3). The decrease in N<sub>2</sub> uptake and specific surface area after the guest loading is reasonable since the partial void spaces of RWY host were occupied or blocked as a result of dye molecules inclusion. The crystallographic data revealed the window of RWY host to be 5.90 Å when taking account of the Van der Waals radii of the pore wall. Such wider window openings, compared to the width of PFH<sup>+</sup> (5.09 Å) and Py<sup>+</sup> (5.09 Å), suggests both dye ions could readily penetrate into the pore space of RWY host. Actually, the single-dye-loaded and dual-dyes-loaded samples were characterized by laser scanning confocal mapping and elemental analysis (Figure 1 and Table S1), which also verified that PFH<sup>+</sup> and Py<sup>+</sup> dye ions were evenly distributed in the pore space throughout RWY host.

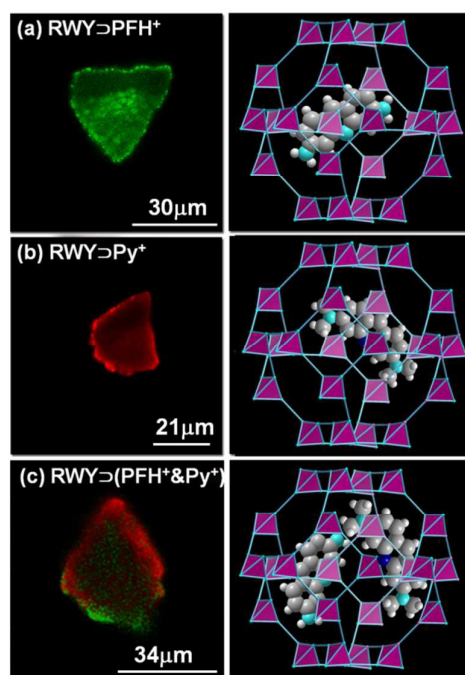


Fig. 1 Confocal laser scanning graphs of dye-loaded RWY in a crosscut single crystal. Both PFH<sup>+</sup> (green) and Py<sup>+</sup> (red) ions can exist in the pore space throughout RWY host.

### Fluorescent characterization of dye-loaded zeolite antennae system

The guest ions in our designed antennae system were carefully chosen in order to construct a proper energy cascade for high-efficiency energy transfer with host-framework involved. Upon excitation at 370 nm, RWY $\supset$ Cs<sup>+</sup> host framework showed a very broad emission band centered at 420 nm (Figure 2a, black curve), whereas the diluted PFH<sup>+</sup> aqueous solution reached its absorption maximum at around 444 nm (Figure 2a, red curve). Meanwhile, the emission spectrum of PFH<sup>+</sup> showed a broad peak centered at 519 nm (Figure 2b, blue curve), which is close to 545 nm where Py<sup>+</sup> chromophore showed its absorption maximum (Figure 2b, pink curve). Each donor-acceptor pair (RWY-PFH<sup>+</sup> and PFH<sup>+</sup>-Py<sup>+</sup>) reached well overlapping in a very wide spectral region. Such wide spectral overlaps in RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) antennae system would greatly facilitate multi-step energy transfer, since the overlaps of absorption band with emission band would in principle favor the fluorescence resonance energy transfer (FRET) caused by the electronic transient dipole moment matching.<sup>12,13</sup>

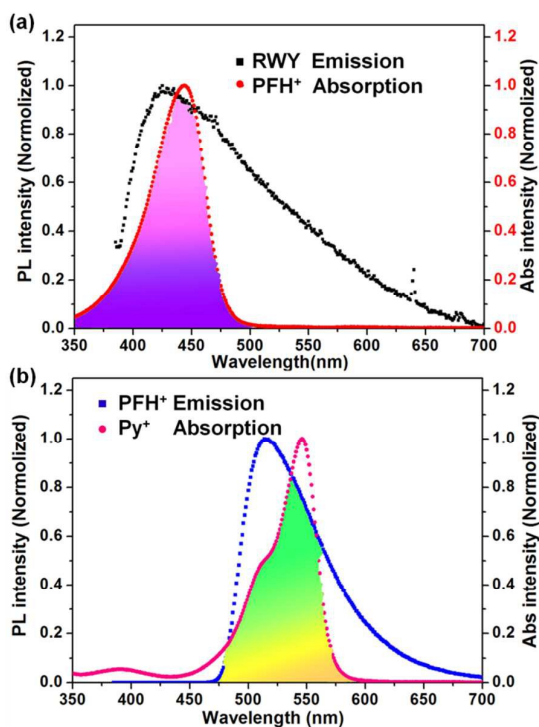


Fig. 2 (a) The overlap of PFH<sup>+</sup> absorption spectrum (red) and RWY emission spectrum (black); (b) The overlap of Py<sup>+</sup> absorption spectrum (pink) and PFH<sup>+</sup> emission spectrum (blue).

The steady-state fluorescence spectra and fluorescence dynamics have been profiled for probing the process of FRET. Figure 3 presented the change of FL spectral features of RWY with or without dye ions under excitation of 370 nm, which can not directly excite both PFH<sup>+</sup> and Py<sup>+</sup> ions for FL emission. In the presence of PFH<sup>+</sup> and PFH<sup>+</sup>-Py<sup>+</sup> coexistence, FL intensity of host RWY at the 420 nm (the diagnostic emission peak of RWY) significantly decreased, indicative of the energy transfer from RWY host to included dye ions. Compared to RWY $\supset$ PFH<sup>+</sup>, RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) host-guest composite showed a further decrease in FL intensity of the maximum emission peak of PFH<sup>+</sup> with appearance of the FL emission band of Py<sup>+</sup> ions, indicating the occurrence of a second-step energy transfer between PFH<sup>+</sup> and Py<sup>+</sup>. It is worth noting that the dynamic fluorescence lifetime of RWY host material at 420nm obviously shortened upon dye molecules inclusion (Figure 4a, Table S2), which also strongly suggests FRET occurs between the RWY host and PFH<sup>+</sup> ions. Similarly, the lifetime of the PFH<sup>+</sup> at 519nm emission experienced obvious decrease after the Py<sup>+</sup> loading (Figure 4b). The variation in relative peak intensity of steady-state FL spectra and the shortened fluorescence dynamics substantially illustrate that the multi-step FRET is achieved in the designed artificial host-guest antenna system.

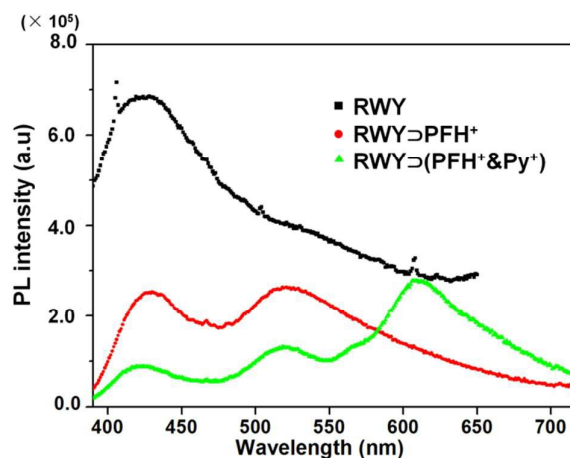


Fig. 3 Steady-state FL spectra of RWY (black), RWY $\supset$ PFH<sup>+</sup> (red), RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) (green) under excitation of 370 nm.

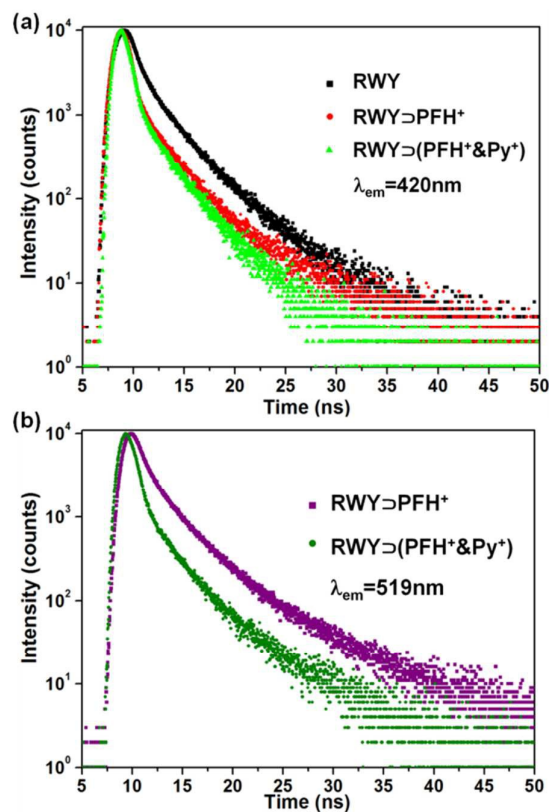


Fig. 4 PL dynamics at different emission wavelengths: (a) RWY, RWY $\supset$ PFH<sup>+</sup> and RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) ( $\lambda_{em} = 420\text{nm}$ ); (b) RWY $\supset$ PFH<sup>+</sup> and RWY $\supset$ (PFH<sup>+</sup>&Py<sup>+</sup>) ( $\lambda_{em} = 519\text{nm}$ )

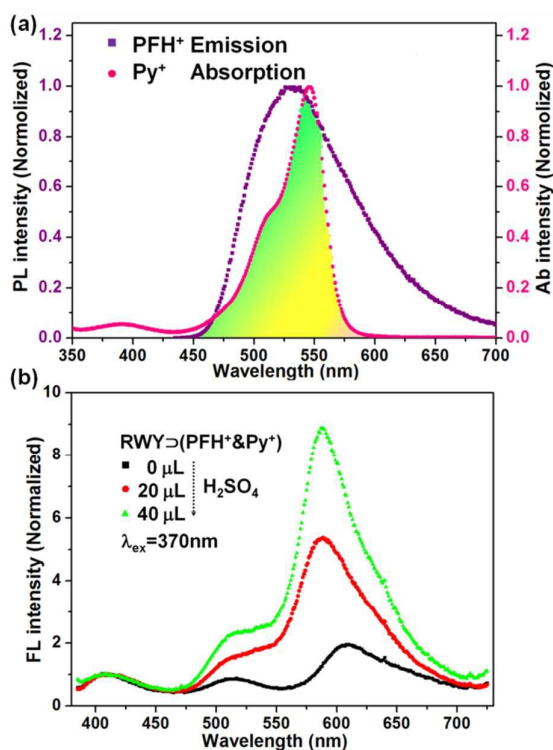


Fig. 5 (a) The overlap of absorption spectrum of  $\text{Py}^+$  (pink) solution and emission spectrum (purple) of  $\text{PFH}^+$  solution treated with  $20 \mu\text{L}$   $\text{H}_2\text{SO}_4$ ; (b) steady-state FL spectra of  $\text{RWY}-(\text{PFH}^+ \& \text{Py}^+)$  treated at different acidity conditions.

#### Effect of acidification of guest $\text{PFH}^+$ on FRET efficiency

The chemical property of proflavine molecule naturally provides stimulant responsive performance since the environmental acidity directly controls the protonation of the amino groups on PF molecules and corresponding optical feature including absorption and emission bands. The different existence forms ( $\text{PF}$ ,  $\text{PFH}^+$  and  $\text{PFH}^{2+}$ ) possess distinctive absorption and emission spectra in either aqueous solutions or solid state. In originally preformed diluted proflavine hemisulfate aqueous solution,<sup>3</sup>  $\text{PFH}^+$  dominated equilibrium mixture shows an absorption band at 444 nm and an emission band at 519 nm. However, under high acidity condition, the  $\text{PFH}^{2+}$  form dominates the solution because two characteristic absorption peaks (345 nm and 360 nm) are observed (Figure S4).<sup>3</sup> Further acidifying  $\text{PFH}^+$  ion leads to a much greater overlap between the  $\text{PFH}^{2+}$  emission spectrum and  $\text{Py}^+$  absorption spectrum due to the red shift of emission peak of  $\text{PFH}^{2+}$  (531 nm, Figure 5a, purple curve), which could further enhance energy transfer efficiency between  $\text{PFH}^{2+}$  and  $\text{Py}^+$ . For a typical  $\text{PFH}^+$  aqueous solution, FL intensity of  $\text{PFH}^+$  ( $I_{\text{PFH}^+}$ ) significantly decreased with  $\text{H}_2\text{SO}_4$  added (Figure S5), and for  $\text{PFH}^+ \text{-Py}^+$  mixed aqueous solution with 1:1 molar ratio, the ratio of  $I_{\text{PFH}^+}/I_{\text{Py}^+}$  changed from greater than 1 for un-acidified solution to less than 1 for acidified solution (Figure S6). However, compared to above solution system, acidified  $\text{RWY}-(\text{PFH}^+ \& \text{Py}^+)$  antenna system displayed different change trend on the ratio of  $I_{\text{PFH}^+}/I_{\text{Py}^+}$  (Figure 5b). On the one hand, the acidified  $\text{RWY}-(\text{PFH}^+ \& \text{Py}^+)$  antenna system exhibited a significant increase in  $I_{\text{PFH}^+}$ , which could be explained that acidification treatment promoted energy transfer from  $\text{RWY}$  to  $\text{PFH}^{2+}$ . On the other hand, the ratio of  $I_{\text{PFH}^+}/I_{\text{Py}^+}$  is always less than 1, which is evaluated to be 0.46, 0.29, 0.26, corresponding to 0L, 20L and 40L  $\text{H}_2\text{SO}_4$  added, respectively (Figure 5b). Moreover, the FL lifetime of

acidified host-guest system showed an obviously shortened tendency for emission at either 420nm or 519 nm (Figure 6 and Table S2). The energy transfer efficiency was promoted from 14% to 33.7% and 29.1% to 37.8% for  $\text{RWY} \text{-PFH}^+$  and  $\text{PFH}^+ \text{-Py}^+$  donor-acceptor pairs, respectively. In a word, deep acidification on  $\text{PFH}^+$  can effectively tune efficiency of energy transfer in both  $\text{RWY} \text{-PFH}^+$  and  $\text{PFH}^+ \text{-Py}^+$  donor-acceptor pairs for the following two major reasons: (1) acidification leads to greater spectra overlapping; (2) more protonation of guest molecule may result in the variation of the electronic dipole moment of guest ions entrapped in the highly negatively charged hosts. To be noticed, acid treatment on  $\text{RWY}$  host does not change its PL property (Figure S7).

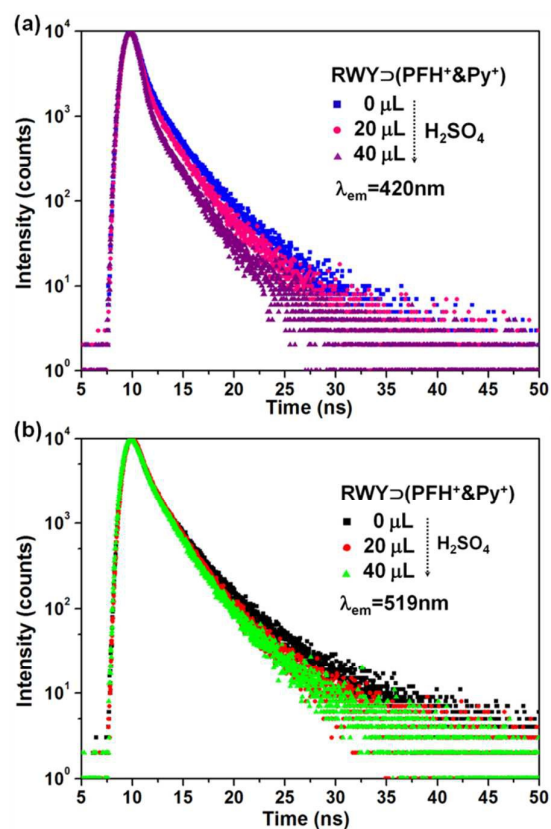


Fig. 6 PL dynamics of emission at different emission center for  $\text{RWY}-(\text{PFH}^+ \& \text{Py}^+)$  host-guest antennae system treated with different amount of  $\text{H}_2\text{SO}_4$ : (a)  $\lambda_{\text{em}}=420\text{nm}$ ; (b)  $\lambda_{\text{em}}=519\text{nm}$ .

#### Solvation effect of guest ions on FRET efficiency

It is generally accepted that the organic solvent molecules surrounding the guest ions not only change the relative orientation of the donor-acceptor transition dipoles, but also affect the distance between donor and acceptor. In addition, the electronic dipole moment of guest molecule can be also accordingly influenced by the polar environment created by polar solvent molecules surrounding the guest.<sup>28, 29</sup> Thus, solvation of guest ions by solvent molecules with different polarity will in principle strongly influence the energy transfer efficiency.

To probe solvation effect on energy transfer efficiency, the solid-state  $\text{RWY}-(\text{PFH}^+ \& \text{Py}^+)$  host-guest antenna systems were fully immersed in the vapor of different organic solvents. Excitation at 370 nm can not directly excite dye ions for FL emission, and the observed visible-light emission from dye ions are totally attributed to energy transfer from host matrix. Therefore, the ratio of  $I_{\text{dye}}/I_{\text{RWY}}$  can

indirectly reflect energy transfer efficiency from light harvester (herein RWY) to energy acceptor (herein dye ions), and higher ratio represents higher efficiency of energy transfer. As shown in Table S3, solvents have little effect on the characteristic FL peak of host RWY, guest PFH<sup>+</sup> and Py<sup>+</sup>. However, the ratio of  $I_{\text{dye}}/I_{\text{RWY}}$  was obviously altered by different solvent molecules, as displayed in Figure 7. It is easily observed that water molecules originally adsorbed in the pore space are not beneficial to energy transfer; rather, other organic solvent, especially ethanol, THF and toluene, drastically promote energy transfer from RWY to PFH<sup>+</sup>, and even from PFH<sup>+</sup> to Py<sup>+</sup>.

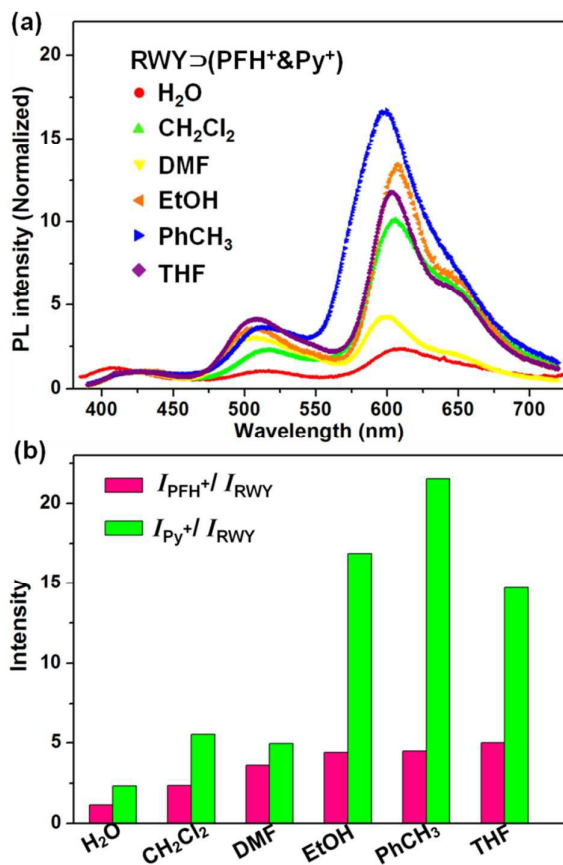


Fig. 7 (a) Steady-state FL spectra of RWY⊃(PFH<sup>+</sup>&Py<sup>+</sup>) antennae system treated with different solvent molecules; (b) Plot of the ratio of  $I_{\text{PFH}^+}/I_{\text{RWY}}$  and  $I_{\text{Py}^+}/I_{\text{RWY}}$ .

## Conclusions

We adopted chalcogenide-based inorganic semiconductor zeolite (RWY) as light-harvesting host and proflavine (PFH<sup>+</sup>) and pyronine (Py<sup>+</sup>) as guests, and successfully fabricated an artificial host-guest antennae system RWY⊃(PFH<sup>+</sup>&Py<sup>+</sup>), in which the multi-step vectorial energy transfer assay was constructed. The ultraviolet high-energy excitations absorbed by RWY host were channeled to PFH<sup>+</sup> ions and then onto Py<sup>+</sup> ions to give rise of visible-light emission. Moreover, effects of the acidification of PFH<sup>+</sup> ion and solvation of guest ion on energy transfer efficiency were also investigated. Further protonation of PFH<sup>+</sup> ion and solvation of guest ions by solvent molecules can dramatically promote energy transfer efficiency in RWY-PFH<sup>+</sup> and PFH<sup>+</sup>-Py<sup>+</sup> donor-acceptor pairs, much higher than that of untreated host-guest antennae system. Current results indicate that the form and peripheral environment of guests

have critical influence in tuning energy transfer efficiency in host-guest antennae system. Such impact factors discussed here need to be further investigated to enhance energy transfer efficiency in current chalcogenide-based host-guest antennae system, and even applied in the study of other host-guest systems.

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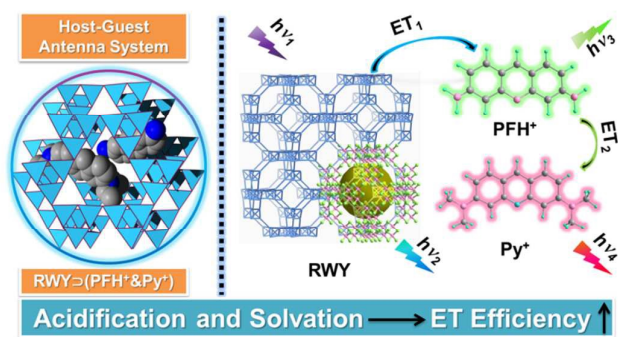
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