Supplementary Information for

Organic-inorganic Hybrid Liquid Crystals of Azopyridines enabled by Halogen Bonding toward Sensor in Aquatic Environment

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1. Synthesis of materials

1.1. Preparation of Ag-AzoPy

The Ag. AzoPy was fabricated according to the recipe described in the literature.¹ AgOAc (0.1 g, in 5.0 ml acetonitrile) and AzoPy (1.0 g) were mixed in a round bottom flask (10 ml) at room temperature. The acetonitrile was removed under vacuum for 30 min. Then, the flask was transferred into an oil bath at the gradually increasing temperature until 130 °C under vacuum. After cooling down to room temperature, the Ag. AzoPy was obtained.

1.2. Preparation of Ag. Br–Br. AzoPy

The Ag. Br–Br. AzoPy was synthesized according to the literature.² The molecular bromine (0.16 g, 1.0 mmol) was added to a solution of Ag. AzoPy (1.0 mmol) in chloroform (5.0 ml). Then the mixture was stirred for 2 h at room temperature. After filtered and dried, the jacinth precipitate was obtained. Then, the di–noncovalent complexes were obtained.

2. TEM



Figure S1. TEM images of Ag...AzoPy (a) and Ag...Br–Br...AzoPy (b), EDS elemental mapping images of Ag...Br–Br...AzoPy for Ag (c) & Br (d) maps.

3. UV-vis absorption spectra

UV-vis absorption spectra of Ag-Br-Br-AzoPy with different mass concentration of Ag NPs were recorded in acetone. As shown in Fig. S2(a), when addition of the concentrations of Ag NPs in Ag-Br-Br-AzoPy from 0 wt% to 20 wt%, the maximum absorption peak of Ag. Br-Br. AzoPy showed red shift from 360 nm to 391 nm. However, when the concentration of Ag NPs in Ag. Br-Br. AzoPy increased to 30 wt%, the maximum absorption peak turned to show blue shift. Fig. S2(b) shows that there are no obviously changes of the UV-vis spectra of AzoPy and Br-Br-AzoPy in acetone when just direct add surface stabilised Ag NPs in a solution by simply physical hybrid method. Different photoresponsive behaviours were obtained in Ag-AzoPy and Ag-Br-Br-AzoPy. Fig. S2(c) shows that the Ag-AzoPy existed a back cis-trans isomerisation by keeping those in the dark at room temperature after UV irradiation. However, for Ag-Br-Br-AzoPy, the maximum absorption peak has a significantly blue shift from 393 nm to 370 nm upon UV irradiation and then could revert to the original state from 370 nm to 382 nm when relaxed in the dark after UV irradiation but do not observed the cis-trans isomerisation phenomenon, which present in Fig. S2(d).



Figure S2. (a) UV-vis spectra of Ag.··Br-Br.··AzoPy with different mass concentration of Ag NPs in acetone. (b) UV-vis spectra of AzoPy and Br-Br.··AzoPy in acetone mixed Ag NPs. (c) and (d) are the UV-vis spectra of Ag.··AzoPy and Ag.··Br-Br.··AzoPy under UV irradiation (at 365 nm) and relaxed in the dark after UV irradiation in acetone.

4. X-ray photoelectron spectroscopy

The N 1s peak of Ag...AzoPy is resolved into two peaks at 399.1 and 400.1 eV, respectively, as shown in Fig. S3(a). The 399.1 eV peak suggests the presence of charged nitrogen atoms, indicating an electrostatic interaction with the silver surface.³ The peak at 400.1 eV is assigned to C–N units, which suggested the interaction between these N atoms and Ag NPs. From the spectrum of Ag 3d peak of Ag...AzoPy (Fig. S3(b)), the binding energies for Ag $3d_{5/2}$ and Ag $3d_{3/2}$ are found to be 374.1 and 368.1 eV, respectively, which are compared to the respective core levels of Ag NPs (374.5 and 368.5 eV), as shown in Fig. S3(d). The results of XPS spectra reveal that the AzoPy has certain interaction with Ag NPs and provided supporting evidence for the structure.



Figure S3. Experimental XPS spectra of (a) N 1s and (b) Ag 3d of Ag...AzoPy. (c) N 1s of AzoPy and (d) Ag 3d core-level spectra of Ag NPs.

5. ¹H NMR and MS analysis





Figure S4. The ¹H NMR spectra of Ag...AzoPy and AzoPy in Acetone–d6 and MS spectrum of Ag...AzoPy.



Figure S5. The ¹H NMR spectra of Ag. Br–Br. AzoPy and Br–Br. AzoPy in Acetone–d6.

The ¹H NMR spectra of samples in Acetone–d6 were examined to further study the interaction between AzoPy, Br–Br···AzoPy with Ag NPs, as shown in Figs. S4–S5. Compared to the pristine molecule AzoPy, the positions of proton b and c of pyridine ring of Ag···AzoPy showed reversal (Fig. S4). In addition, the Ag···Br–Br···AzoPy exhibit an obvious downfield shift in their chemical shift compared to the pristine molecule Br–Br···AzoPy (Fig. S5). These remarkable evidences undoubtedly indicate

the strong actions between these samples and Ag NPs, leading to the formation of metal nanoparticles composites which could be generate an exciting phenomenon.

6. POM images



Figure S6. POM images of 12Br and 12Br–Ag in parallel orientation cell (a & c), with the cell rotated through 45° to the left (b & d) after annealing treatment at room temperature. (e & g) and (f & h) are 12Br and 12Br–Ag in parallel orientation cell and after sample rotation between crossed polarizers 45° to the left in liquid crystal temperature.

POM images of 12Br-Ag in the rubbed polyimide ITO glass cells showed homogenous planar alignment with no aggregation regardless of rotating the LC cell after annealing treatment at room temperature in Figs. S6(c, d), similar to the non-doped halogen-bonded liquid crystal 12Br in Figs. S6(a, b). Differently, the 12Br-Ag is hardly to orientation by the alignment layers of the cell in liquid crystal temperature, as shown in Figs. S6(g & h). This suggests that the directing abilities of the Ag NPs are selective to surpass that of the alignment layers of the cell according to the temperature condition. Although no texture change while a clear birefringence change was observed in 12Br-Ag when the d/l ratio decreased compared to 12Br, as shown in Fig. S6(g). The above observations imply that the doping with Ag NPs in liquid crystal plays a dominant role in changing the birefringence by decrease the d-spacing and inhibit orientation.

7. Polarized UV-Vis spectra



Figure S7. Polarized UV–Vis spectra of 12Br (a) and 12Br–Ag (b) films with parallel orientation. The black and red curves are the absorption parallel and perpendicular to the orientation direction, respectively.

Moreover, the aligned mesogens 12Br show strong anisotropy in their polarized UV-vis absorption spectra and the orientation factor is 0.049. However, the organic-inorganic hybrid liquid crystals 12Br-Ag have a low order degree which the orientation factor is 0.011.

8. Metal-enhanced fluorescence



Figure S8. (a) Fluorescence emission spectra of AzoPy, Br–Br···AzoPy, Ag···AzoPy and Ag···Br–Br···AzoPy. Dependences of fluorescence emission spectra on the quantity of nanoparticles in Ag···AzoPy (b), Ag···Br–Br···AzoPy (c) and upon UV irradiation (d) in acetone solution, the mass concentrations of composites were 0.6 wt% in acetone. (e) Schematic illustration of fluorescence processes in the Ag···AzoPy and the Ag···Br–Br···AzoPy composites under excitation at 352 and 393 nm.

To investigate the occurrence and intensification of MEF of AzoPy, we studied the fluorescence emission of the free AzoPy ligand and their corresponding complexes with Ag NPs. Fig. S8(a) shows the fluorescence spectra of AzoPy, Br–Br…AzoPy,

Ag···AzoPy nanoparticles, and Ag···Br–Br···AzoPy nanoparticles with the same concentration (0.6 wt%) in acetone. In contrast to AzoPy, the fluorescence intensity of Br–Br···AzoPy was much weaker, which is associated with the heavy atom effect caused by the molecular bromine.¹ However, significant enhancement of fluorescence of AzoPy was observed upon formation of Ag···AzoPy and Ag···Br–Br···AzoPy nanoparticles compared to AzoPy and Br–Br···AzoPy. This dramatic enhancement of fluorescence results from the presence of Ag NPs in these systems through the MEF phenomenon.⁴ It is important to note that the fluorescence intensity of organic–inorganic hybrid Ag···Br–Br···AzoPy nanoparticles enabled by halogen bonding was approximately three times higher than that of Ag···AzoPy nanoparticles. This implies that the insertion of Br₂ between the AzoPy ligand and Ag NPs intensifies the MEF of the ligand. This interesting characteristic is attributed to the increased distance between the azodye molecule and Ag NP surface due to the presence of the intervening Br₂. As shown in Fig. S9, MM2 molecular mechanics calculations support this hypothesis.

The influence of concentration of Ag NPs on the fluorescence enhancement effect was studied in detail, as shown in Figs. S8(b) and S8(c). Both Ag...AzoPy and Ag...Br-Br...AzoPy exhibited their fluorescence emission in the wavelength range of 450–700 nm. However, only one emission maximum appeared at about 570 nm as shown in Fig. S8(b), due to the MEF effect of Ag...AzoPy, which was further enhanced with increase in the amount of Ag NPs. Differently, a shoulder peak at around 533 nm got stronger in Ag...Br-Br...AzoPy upon the increase of Ag NPs (Fig. S8(c)), which might be result from more efficient formation of hybrid Ag NPs. The broad peak at around 575 nm in Fig. S8(c) can be ascribed to the remaining Ag...AzoPy, which are not involved in the di-noncovalent reaction. In addition, the fluorescence emission spectra of Ag...AzoPy and Ag...Br-Br...AzoPy under UV irradiation (365 nm) were studied. The intensity of the fluorescence emission of both was reduced upon UV irradiation. This may be due to disturbance in bonding among Ag, N and Br by UV irradiation which is consistent with the result of the UV-vis spectrum (Fig. S2(d)).

When the Ag NPs doping is up to 50 wt% AzoPy and Br-Br···AzoPy, respectively, the concentration of both Ag...AzoPy and Ag...Br-Br...AzoPy nanoparticles were 0.6 wt% in acetone, we estimated a fluorescence increase as high as approximately 25 times for Ag. AzoPy nanoparticles and 320 times for Ag. Br-Br. AzoPy nanoparticles compared to that of pure organic materials AzoPy and Br-Br. AzoPy, respectively, as shown in Figs. S8(b) and S8(c). The high enhancement effect observed on the metallic nanoparticles is due to the fluorophore dipole interacting with free electrons in Ag NPs,^{5,6} offering promise for a range of applications in chemical and biological sensing.^{7,8} In addition, the emission peaks underwent obvious blue shift from 570 to 545 and 538 to 533 nm as the amount of nanoparticles in Ag...AzoPy (Fig. S8(b)) and Ag...Br-Br...AzoPy solutions increased from 10 wt% to 50 wt% (Fig. S8(c)). Similar behaviour has been previously observed in Ag-SiO₂-FITC core-shell nanoparticles, which can be explained by the dielectric environment change upon increasing the concentration of Ag NPs, induced by the spectral overlap of Ag plasmon band with the absorption spectra of AzoPy and Br-Br···AzoPy.9

9. Computational details

The MM2 program offered significant insights into the noncovalent intermolecular interactions helping to illustrate the distance between dye and Ag NPs. Here, we have undertaken a theoretical study of the entire process of formation of 1:1 stoichiometry dye/Ag NPs structures, in order to contribute to the understanding and rationalization of fluorescence experimental results. As shown in Fig. S9, the distances between dye and Ag NPs in an ascending order are 0.2 nm and 0.66 nm for Ag···AzoPy and Ag···Br–Br···AzoPy, respectively.



Figure S9. Calculated distances of Ag.··AzoPy (a), Br–Br.··AzoPy (b), Ag.··Br–Br.··AzoPy (c) and the distances between dye and Ag NPs for Ag.··AzoPy and Ag.··Br–Br.··AzoPy.

10. The fluorescence spectral testing



Figure S10. (a) Dependences of fluorescence emission spectra on excitation with different wavelengths of Ag...Br–Br...AzoPy in acetone. The fluorescence emission spectra of Ag NPs, directly mixed Br–Br...AzoPy and Ag NPs in solution and *in situ* synthesis of Ag NPs in Br–Br...AzoPy (b), Ag...AzoPy (c) and Ag...Br–Br...AzoPy (d) with different mass concentration in acetone.

The fluorescence intensity of both $Ag \cdots AzoPy$ and $Ag \cdots Br - Br \cdots AzoPy$ nanoparticles was intensified with increasing their concentration in acetone (Figs. S10(c) & (d)). The fluorescence emission spectra of $Ag \cdots Br - Br \cdots AzoPy$ nanoparticles on excitation with different wavelengths, Ag NPs, mixed $Br - Br \cdots AzoPy$ and Ag NPs directly in solution and *in situ* synthesis of Ag NPs in $Br - Br \cdots AzoPy$ were also tested (Figs. S10(a) & (b)).

The fluorescence spectra of Ag. Br–Br. AzoPy excited by different excitation wavelength in the reign from 360 to 410 nm were investigated, as shown in Fig. S10(a). When the excitation wavelength located at 360 nm, there is only one main peak at around 560 nm in the fluorescence emission spectra. However, when the excitation wavelength increased to 370 nm, another peak appeared at shorter wavelength and its intensity increased accompanying with continued increasing the

excitation wavelength from 380 to 390 nm. When the excitation wavelength is longer than 390 nm, the intensity of fluorescence emission spectra and the location did not change with the excitation wavelength increased to 410 nm. At last, the peak at around 535 nm became the main peak. It is suggested that the Ag. Br-Br. AzoPy would exist two emitting centers, which belong to Ag-Br-Br-AzoPy and Ag-AzoPy, the fluorescence intensity of respectively. Meanwhile, Ag…AzoPy and Ag-Br-Br-AzoPy increased with increasing the mass concentration of Ag. Br-Br. AzoPy and Ag. AzoPy in acetone, as shown in Figs. S10(c) & (d). The SPR of Ag NPs located at 390 nm, while just mixed Br-Br-AzoPy and Ag NPs directly in solution and in situ synthesis of Ag NPs in Br-Br-AzoPy could not obviously enhance the fluorescence (Fig. S10(b)).

11. Fluorescence quantum yield



Figure S11. Fluorescence emission spectra of AzoPy (a,b), Ag. AzoPy (c,d), Br-Br. AzoPy (e,f), Ag. Br-Br. AzoPy (g,h) before and after UV irradiation and remove UV irradiation. And their excitation at 343, 357, 353 and 353 nm, respectively.

Compounds	AzoPy	Ag····AzoPy	Br-Br···AzoPy	Ag····Br-Br····AzoPy	Rhodamine B
$\Phi_{ m f}$	0.080	0.100	0.051	0.107	0.900

Table S1. Measured fluorescence quantum yield (Φ_f).

We have evaluated the fluorescence quantum yield and fluorescence lifetime of the azodye functionalised Ag NPs. MEF is known to occur *via* an increase of the intrinsic decay rate for a fluorophore near a metal surface.⁵ In this case, the quantum yields of Ag···AzoPy and Ag···Br–Br···AzoPy nanoparticles are 0.1, and 0.107, respectively, as shown in Fig. S11 and Table S1. As the value of quantum yield increased, the fluorescence lifetime decreased. As a result, the lifetime of the fluorophore would be shortened, which is consistent with the results shown in Fig. S12. This result strongly suggests the occurrence of the metal–fluorophore near–field interaction.

12. Fluorescence lifetime

In this case, the lifetimes were derived from the time traces using time corrected single-photon counting (TCSPC) technique and analyzed in terms of a triple-exponential decay (Fig. S12). The average lifetimes of AzoPy and Br-Br...AzoPy fluorophore were estimated to be 1.68 and 2.17 ns, respectively, in the absence of Ag NPs, which decreased to 1.64 and 1.52 ns with 10% Ag NPs. This trend observed in the shortening of lifetime is important evidence to confirm the metal-fluorophore interaction, which is consistent with the intensity enhancement on the metal particles.



Figure S12. Emission decay curves of AzoPy and Br–Br…AzoPy in the absence of Ag NPs and presence of Ag NPs.

References

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