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Water-dispersible donor-acceptor-donor π-conjugated bolaamphiphiles enabling a humidity-responsive luminescence color change

Novel organic donor-acceptor-donor π-conjugated fluorophores that are dispersible in water have been developed. By doping one of the molecules into a hydrophilic polymer, a composite material displaying a humidity-responsive luminescence color change has been fabricated.

See Youhei Takeda et al., Chem. Commun., 2024, 60, 3653.
Water-dispersible donor–acceptor–donor \( \pi \)-conjugated bolaamphiphiles enabling a humidity-responsive luminescence color change†

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Novel water-dispersible donor–acceptor–donor \( \pi \)-conjugated bolaamphiphiles, having dibenzo[\( \pi \)]phenazine as the acceptor and heteroatom-bridged amphiphilic diarylamines as the donors, have been developed. The materials display a distinct photoluminescence color change in response to humidity in a poly(vinylalcohol) matrix.

Organic hydrophobic \( \pi \)-conjugated compounds have found promising applications in the optoelectronics field, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), organic lasers (OLS), organic light-emitting transistors (OLETs), and organic photovoltaics (OPVs), due to their electro- and/or photo-active functions arising from the delocalized \( \pi \)-electrons over the entire molecule. However, their use has been severely limited in a non-aqueous environment, due to their intrinsic hydrophobic nature. In contrast, amphiphilic \( \pi \)-conjugated organic molecules, which have a hydrophobic \( \pi \)-conjugated core and amphiphilic/hydrophilic chains, have recently emerged as a new class of functional materials. Amphiphilic nature allows self-assembly of molecules in an aqueous environment to form diverse supramolecular morphologies such as micelles, vesicles, fibers, nanotubes, and H-/J-aggregates, etc., and being complementary to hydrophobic \( \pi \)-conjugated units and dispersibility in water, they can open up new horizons of materials applications in aqueous environments, such as bio-electronics, bio-imaging, photodynamic therapy, and aqueous photo-catalysis.

Herein, we disclose the development of novel \( \pi \)-conjugated bolaamphiphiles 1–4 that have an electronic donor–acceptor–donor (D–A–D) architecture \( (D = \text{phenoazine}: \text{POZ} \text{and phenothiazine}: \text{PTZ}) \) at the central core and six amphiphilic triethylene glycol monomethyl ether \( (\text{TEGME}) \) and branched polyl units at both edges of the donors (Fig. 1). By making use of the dispersibility in water and charge-transfer (CT) excited state, a humidity-responsive photoluminescence (PL) color change in a hydrophilic polymer film was demonstrated.

To design amphiphilic functional molecules, a DBPHZ-cored D–A–D structure \( (A = \text{DBPHZ}, D = \text{POZ and PTZ}) \) has been chosen as the photoluminescent \( \pi \)-conjugated core, as it exhibits distinct PL arising from the CT excited state. Given that the intensity and wavelength of CT emission is highly sensitive toward the polarity of the microenvironment around the material, humidity detection with amphiphilic D–A–D compounds would be feasible. Furthermore, depending on the population of the predominant conformation of the D–A–D compound with the PTZ donor, the ratio of emissions from local excited
Aquatic environment. Negatively stained transmission electron microscopy revealed that the moderate stability of the nanoparticles in an aqueous environment was suggested by an electrophoretic light scattering (ELS) method to be further investigated. Since the size distribution of nanoparticles was evaluated by molecular dynamics (MD) simulation (vide infra), which is illustrated in Fig. 3b along with the hierarchical assembly structure.

By utilizing the dispersibility in water, UV-Vis absorption spectra of compounds 1–4 in aqueous environments were investigated (Fig. 2). Overall, the spectra of an aqueous solution of 1–4 (solid lines) resembled those in THF (dotted lines), along with a slight red-shift of the spectra (Fig. 2). This observation indicated that D–A–D compounds weakly interact with each other within its self-assembly architecture, although the contribution of solvatochromism is not totally excluded. It should be noted that the absorption spectra of PTZ-bearing compounds 2 and 4 displayed more distinct CT absorption at around 440 nm than their POZ-analogues. This distinct difference is ascribed to the conformational fluctuation of 2 and 4 in the ground state arising from the varied orientation of a substituent on the nitrogen atom of the PTZ donor (i.e., equatorial or axial). Whereas the D–A–D compounds having a POZ donor (i.e., 1 and 3) adopt almost an orthogonal D–A dihedral angle conformation, the D–A–D compounds having a PTZ donor (i.e., 2 and 4) adopt an admixture of axial–axial, axial–equatorial, and equatorial–equatorial conformers.

The admixture nature of the conformers for 2 was supported by molecular dynamics (MD) simulation, which was performed for the system in which there are an equal number of molecules of axial–axial and equatorial–equatorial conformers of 2 in water (Fig. 3, Fig. S6, and movie in the ESI†). After the equilibration run, the molecules were spontaneously assembled and formed (USAXS and SAXS) measurements in aqueous solutions of 1–4 revealed that the D–A–D compounds form large hierarchical assemblies (>100 nm) composed of small aggregates (i.e. subunits) with radii of gyration ($R_g$) ranging from 3.5 to 5 nm (Fig. 3a and Fig. S5, ESI†). The size of the subunits is rationalized by molecular dynamics (MD) simulation (vide infra), which is illustrated in Fig. 3b along with the hierarchical assembly structure.

![Fig. 1](https://example.com/fig1.png)

**Fig. 1** Chemical structures of bolaamphiphiles 1–4.

![Fig. 2](https://example.com/fig2.png)

**Fig. 2** UV-Vis absorption spectra of (a) 1, (b) 2, (c) 3, and (d) 4 in THF (dotted lines) and an aqueous medium (solid lines).
Although the PLQY is still under the detection limit (Fig. 4a). It is worth mentioning that PTZ-containing compound 2 was quenched in a H2O-THF medium (PLQY was under the detection limit of 0.01). In contrast, compounds 3 and 4, which have branched polyol wings at the edge, displayed distinct PL spectra under a relatively high concentration (c = 10^{-4} M), although the PLQY is still under the detection limit (<0.01). The PL are detectable by even the naked eye under UV light (Fig. 4a). It is worth mentioning that PTZ-containing compound 4 displayed a broad dual emission at \(\lambda_{em} = 533\) and 647 nm, while the POZ analogue 3 displayed a Gaussian type PL spectrum peaked at \(\lambda_{em} = 660\) nm (Fig. 4a). The observed dual emission would indicate that different conformers of molecule 4 (ax-ax, ax-ee, and eq-ee) are retained even in the excited state in the self-assembly, which was supported by the different excitation spectra in water (Fig. S7, ESI†). It should be noted that the dual emission of 4 was only observed in water. In polar organic solvents (c = 10^{-4} M in DMSO and DMF), compounds 3 and 4 exhibited emission peaked at around \(\lambda_{em} = 540\), absent in the lower-energy emission (Fig. S8, ESI†). Given that the orientation polarizability (Δf) of water (0.32) is much higher than that of DMSO (0.27) and DMF (0.28), the only lower CT excited state of 4 (excited state for an equatorial-oriented conformer) in polar organic solvents was likely dissipated (Fig. S8, ESI†).

By making full use of the water-dispersible nature of compounds 1 and 2, homogeneous films (1@PVA and 2@PVA) were fabricated through casting a solution of admixture of water-soluble polymer, poly(vinylalcohol) (PVA), and 1 and 2 (1 wt%) on a quartz plate followed by drying (Fig. 4). Notably, both films 1@PVA and 2@PVA displayed distinct PL, which were more visible by the naked eye when compared with PL in solution (Fig. 4b–d). In contrast to 1 and 2, the PL of compounds 3 and 4 was quenched in the solid state (PLQY < 0.01), probably due to quenching of the excited states by hydroxy groups of the neighboring amphiphilic polyol units through energy transfer to a high-energy vibration level.19 Thus, only compounds 1 and 2 were applied for the preparation of PVA films. Film 1@PVA displayed orange-to-red emission with a single peak (\(\lambda_{em} = 642\) nm, \(\Phi_{PL} = 0.04\)) (Fig. 4b), while film 2@PVA exhibited yellowish orange emission with double peaks (\(\lambda_{em} = 533\) and 627 nm; \(\Phi_{PL} = 0.06\)). The dual emission from PTZ-containing 2@PVA should also be ascribed to the presence of different conformers arising from the orientation of the substituent on the nitrogen atom of the donor unit, as suggested by the MD simulation (Fig. 3). Importantly, the PL spectra of the composite films respond to humidity (Fig. 4b–d). After the exposure of 1@PVA...
film to water vapor for 1 h in a bottle filled with NaCl aq. (RH 75%),20 the emission intensity decreased (Fig. 4b). Intriguingly, in the case of 2@PVA, only the intensity in the lower-energy emission band was decreased in response to humidity (Fig. 4c). This indicates that the film containing D–A–D compound 2 displayed a much stronger increase in absorbance in the O–H stretching band (3000–3000 cm⁻¹) upon exposure to water vapor compared to its counterpart. This suggests that the thickness of the film containing D–A–D compound 2 was much thinner than that of the PVA film due to the lower hydrophilic character of the film (Fig. S10a, ESI†). The PVA film displayed a much broader absorption band over the O–H stretching region (3000–300 cm⁻¹) (Fig. S10b, ESI†). The film containing D–A–D compound 2 displayed a more significant increase in absorbance than PVA only, indicating the higher hydrophilic character of the film (Fig. S10a, ESI†). The PVA film shows double-peaked absorption at around 3400 cm⁻¹ and 3600 cm⁻¹ (Fig. S10b, ESI†), which would be ascribed to the O–H stretching bands of isolated water molecules weakly bound to the materials and of small water clusters formed with a few molecules, respectively. In contrast, the film containing D–A–D compound 2 displayed a much broader absorption band over the O–H stretching region (3000–3700 cm⁻¹) (Fig. S10a, ESI†). This would indicate that water molecules existing around the film containing 2 form larger clusters like intermediate water than those in the PVA film.22 Although the detailed mechanisms await further studies, it is conceivable that the loss of flexibility of water molecules in rotation and motion by forming a hydrogen bonding network through the OH group of PVA, water molecules, and TEGME groups in 2 led to the suppression of non-radiative decay and the manifestation of photoluminescence in the PVA films.

In summary, novel water-dispersible π-conjugated bolaamphiphiles have been developed. The materials form nm-size self-assemblies and display photoluminescence in a water environment. Furthermore, composite films with PVA allow for not only photoluminescence but also visualization of humid environments by the naked eye.

We acknowledge a Grant-in-Aid for Scientific Research on the Innovative Area “Aquatic Functional Materials: Creation of New Materials Science for Environment-Friendly and Active Functions” (JSPS KAKENHI Grant Numbers JP19H05716, JP20H05198, JP22H04531, JP19H05718, JP19H05721, JP19H05717, JP22H04541) and a Grant-in-Aid for Scientific Research (B) (JP23H02037). This work was partially supported by JSPS KAKENHI Grant Number JP23H04878 in a Grant-in-Aid for Transformative Research Areas “Materials Science of Meso-Hierarchy”. We acknowledge the Administrative Group of “Aquatic Functional Materials” for supplying D₂O for DOSY experiments (JSPS KAKENHI Grant Number JP19H05714). The synchrotron radiation experiments were performed at the BL19B2 beamline of SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No. 2021A1628, 2022A1797, 2022B0578, and 2022B1963). The computations were partially performed at the Research Center for Computational Science, Okazaki, Japan (Project: 22-IMS-C043 and 23-IMS-C038).

Conflicts of interest
There are no conflicts to declare.

Notes and references
18. Although the diffusion-ordered NMR spectroscopy (DOSY) experiment of 1 was tried in D₂O, distinct resonance signals were not detected, probably due to the low-solubility in D₂O.