

Anion induced modulation of self-assembly and optical properties in urea end-capped oligo(*p*-phenylenevinylene)s†

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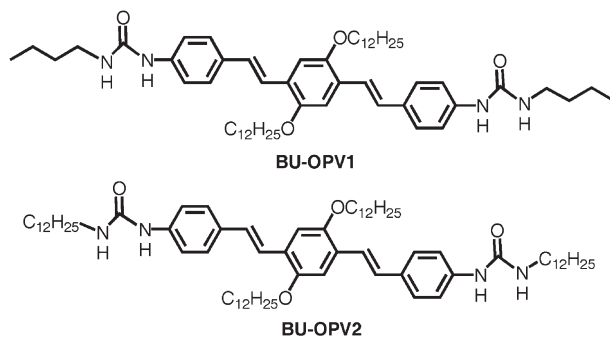
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The non-emissive supramolecular assembly of urea end-capped oligo(*p*-phenylenevinylene) fluorophores turned strongly emissive in the presence of tetrabutylammonium fluoride which has implications in the anion controlled design of supramolecular architectures with tunable emission properties.

Design of functional supramolecular architectures is one of the main goals of interdisciplinary research in chemistry, biology and material science. Toward this end, control on the supramolecular assemblies of oligo(phenylenevinylene)s (OPVs) is at the centre stage of research.^{1,2} Recently, we have reported the gelation of OPVs and the resultant modulation of optical properties for the purpose of selective light harvesting.³ Here we report on the construction of supramolecular stacks of bisurea end-capped OPVs and their anion induced destruction leading to a remarkable modulation of the emission behavior thereby opening the avenue for the anion controlled modulation of supramolecular architectures with tunable optical properties.



The bisurea tethered OPVs, **BU-OPV1** and **BU-OPV2**, have been synthesized by a multistep synthetic strategy adopting standard procedures and characterized by spectral analyses (see ESI†). The UV/Vis spectra of **BU-OPV1** in chloroform (1×10^{-5} M, $\epsilon = 6.22 \times 10^4$ M⁻¹ cm⁻¹) showed characteristics of molecularly dissolved OPVs indicating that they are not aggregated in chloroform (Fig. 1(a)). However, in non-polar solvents such as cyclohexane, the UV/Vis spectrum of **BU-OPV1** (1×10^{-5} M) is broad with an absorption maximum at 410 nm ($\epsilon = 9.59 \times 10^3$ M⁻¹ cm⁻¹) with a shoulder band at 460 nm ($\epsilon = 5.4 \times 10^3$ M⁻¹ cm⁻¹), characteristic of self-assembled OPV chromophores. The fluorescence spectrum of **BU-OPV1** in

chloroform (1×10^{-5} M) showed a strong emission maximum at 454 nm with a shoulder at 487 nm ($\Phi_f = 0.35$) (Fig. 1(b)). However in cyclohexane, the fluorescence of **BU-OPV1** is significantly quenched ($\Phi_f = 0.02$) indicating strong intermolecular interactions between OPVs which is a thermoreversible process as revealed by temperature dependent emission studies (Fig. 1(b), inset). The **BU-OPV1** aggregates remain stable up to a dilution of 10^{-7} M and up to 60 °C as indicated in the absorption and emission changes. Based on the above observations it is clear that **BU-OPV1** forms a stable one-dimensional assembly by the cooperative interaction of H-bonding between the urea groups and π -stacking between the aromatic moieties.⁴

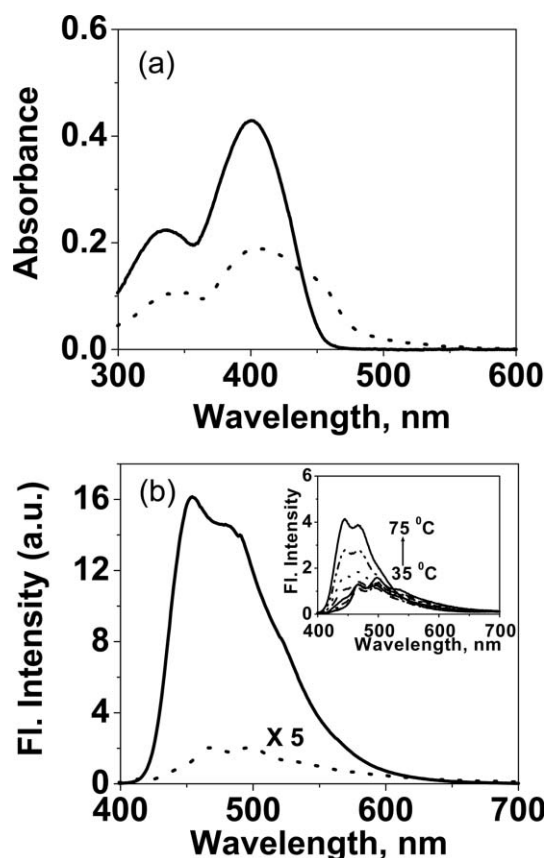


Fig. 1 (a) Absorption and (b) emission spectra of **BU-OPV1** (1×10^{-5} M) in cyclohexane (···) ($\Phi_f = 0.02$) and in chloroform (—) ($\Phi_f = 0.35$). The emission spectrum in cyclohexane is zoomed 5× to make it visible. Inset: Changes in the emission ($\lambda_{ex} = 380$ nm) spectra in cyclohexane with increasing temperature.

† Electronic supplementary information (ESI) available: Spectroscopic data, Benesi–Hildebrand plots, synthesis and characterization of **BUOPVs** and experimental procedures. See <http://www.rsc.org/suppdata/cc/b413909g/>

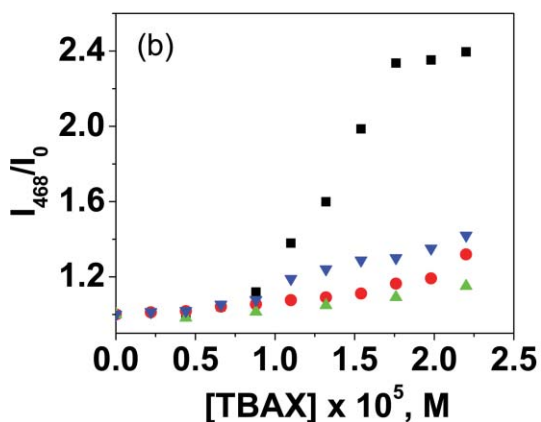
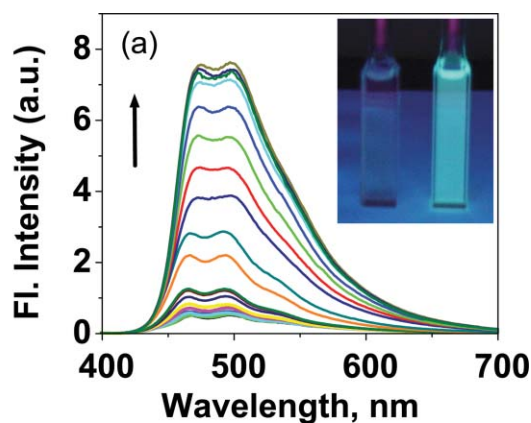


Fig. 2 (a) Changes in the emission spectra of **BU-OPV1** (1.1×10^{-5} M) in cyclohexane–chloroform (16:1) upon the addition of TBAF (2.2×10^{-6} – 3.96×10^{-4} M). Inset: photograph under UV light showing strong emission of **BU-OPV1** in the presence of TBAF. Emission of **BU-OPV1** (left) and emission of the **BU-OPV1**·TBAF complex (right). (b) Fluorescence intensity of **BU-OPV1** (1.1×10^{-5} M) at 468 nm upon titration with 0–2 equivalents of quaternary ammonium halides (TBAX); TBAF (■), TBAC (▼), TBAB (●), TBAI (▲).

Since halide anions are known to compete with urea H-bonds,^{5,6} we were keen to know whether anions can induce the breaking of the H-bond and π -stack assisted self-assembly of **BU-OPV1** and **BU-OPV2** thereby reinstating the strong emission of the **OPV** units. Fig. 2(a) shows the fluorescence enhancement observed when the **BU-OPV1** self-assembly is titrated with increasing amounts of tetrabutylammonium fluoride (TBAF). A gradual increase in the TBAF concentration up to 28 equivalents relative



Fig. 3 Interaction of F^- with the **BU-OPV1** self-assembly which justifies the enhancement in fluorescence.

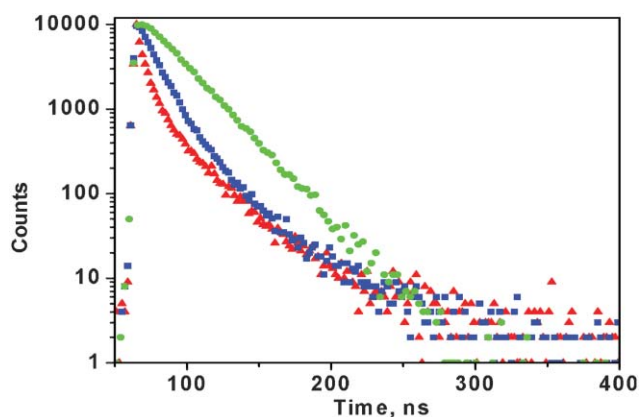


Fig. 4 Time resolved fluorescence decay profiles of **BU-OPV1** in chloroform (●), cyclohexane–chloroform (16:1) (▲) and after the addition of 30 equivalents of TBAF (■).

to the concentration of **BU-OPV1** (1.1×10^{-5} M) resulted in a 14-fold fluorescence enhancement, with saturation being observed after the addition of *ca.* 32 equivalents.

The effect of F^- on **BU-OPV1** was visible by the naked eye due to the strong fluorescence upon illumination with a UV lamp (Fig. 2(a), inset). However, for chloride, bromide and iodide ions, the enhancement in fluorescence is relatively weak, particularly for iodide ions. This is clear from plots of the emission changes at 468 nm as a function of the salt concentration, which show higher selectivity for F^- over other halide ions, especially at low concentrations of halide anions (10–20 μ M) (Fig. 2(b)). The selectivity of the **BU-OPV1** self-assembly to anions was found to be in the order $F^- > Cl^- > Br^- > I^-$ which is rationalized on the basis of anion basicity. Fluoride ions being more basic than the other halide ions, will form strong hydrogen bonded complexes with the **BU-OPV1** self-assembly. **BU-OPV2** is found to exhibit a similar selectivity for fluoride ions.

The observed quenching of the emission in cyclohexane and the anion induced recovery as shown in Fig. 2 is rationalized on the basis of the one-dimensional stacking and destacking of the **OPVs** as shown in Fig. 3. At the initial stages of addition, the fluorescence titration curve could be fitted well to a 1:1 binding isotherm, indicating the formation of a 1:1 complex (see ESI†). The persistence of the vibronic shoulder of the self-assembled species at 460 nm and the resemblance of the excitation spectrum of **BU-OPV1** with the absorption spectrum after the addition of 2 equivalents of TBAF suggest strong chromophore interactions in the resulting 1:1 complexes. The Benesi–Hildebrand plot of the

change in the emission intensity against the reciprocal of the TBAF concentration gave a linear fit, characteristic of a 1:1 complexation from which the association constants is estimated as $2.8 \times 10^4 \text{ M}^{-1}$. However, an increase of TBAF concentration beyond 2 equivalents results in a dramatic increase in the fluorescence and the Benesi–Hildebrand plots beyond 2 equivalents could be fitted to the binding isotherm of a 1:2 stoichiometry, which gave a binding constant of $5.1 \times 10^7 \text{ M}^{-2}$. At this situation, a gradual increase in the absorbance at 410 nm with the disappearance of the shoulder band corresponding to the self-assembly at 460 nm was observed in the UV/Vis spectra indicating a complete breaking of the OPV stacks (see ESI†). Thus, with the increase of TBAF concentration, the 1:1 stoichiometry of the sandwich complex gradually changes to a 1:2 stoichiometry with no interchromophore interactions (Fig. 3(c)), thereby exhibiting a high quantum yield of emission ($\Phi_f = 0.32$).

Time-resolved single photon counting experiments (Fig. 4) of **BU-OPV1** in chloroform showed a single exponential decay with a lifetime of 1.32 ns ($\chi^2 = 1.03$) corresponding to the non-assembled **BU-OPV1**. In cyclohexane, a multiexponential fit ($\chi^2 = 1.11$) corresponding to lifetimes of 0.19 ns (36.89%), 0.67 ns (41.64%) and a relatively long-lived species (1.96 ns, 21.47%) could be obtained, indicating the presence of self-assembled species. Upon addition of 30 equivalents of TBAF to **BU-OPV1** the behavior was best reproduced by a biexponential fit ($\chi^2 = 1.1$) in which the major fraction corresponds to a lifetime of 0.66 ns (82.43%) with a minor contribution of a longer-lived species corresponding to 1.79 ns (17.59%). These observations clearly show that F^- ions enter into a competitive H-bond interaction with the urea groups, thereby disrupting the supramolecular stacks of the **BU-OPV1** and thus restoring the strong emission.

In conclusion, we have demonstrated a novel supramolecular approach to “turn off” and “turn on” the emission of OPV self-assemblies, taking advantage of the competitive H-bonding interaction of halide ions with urea groups. We are currently exploring the possibilities of using this idea in controlling the morphology and optical properties of OPV based nanoarchitectures.

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