Controlling the energy-transfer direction: an oligophenylenevinylene–phenanthroline dyad acting as a proton triggered molecular switch

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In a two-component system combining an oligophenylenevinylene (OPV) group with a protonable phenanthroline unit, the direction of intercomponent photoinduced energy transfer can be tuned by proton input, thus allowing on/off switching of the luminescence of the OPV moiety.

A molecular switching device exists in two (or more) different states that can be reversibly interconverted and present different characteristic properties.[1–4] Typically, the switching work is carried out by photons, electrons, or external chemical species.[3] Of course it is crucial to be able to distinguish between the different states, and one of the most powerful tools is fluorescence spectroscopy.[2] For instance, a large variety of molecular recognition events taking place on molecular receptors has been revealed by switching or tuning the luminescence of nearby signaling moieties.[2,3,5]

Oligophenylenevinylenes (OPVs) are strongly fluorescent molecules widely used in materials science for the preparation of light emitting devices (LEDs), field-effect transistors (FETs) or photovoltaic cells.[6,7] Such compounds appear also to be attractive functional building blocks for the construction of new molecular and supramolecular photoactive devices. Here, we describe the preparation and the electronic properties in CH_2Cl_2 solution of the two-component array 3PV-Phen, combining an OPV unit with a protonable phenanthroline group. The related compounds 3PV[8] and Phen have been used as reference compounds for the photophysical studies.
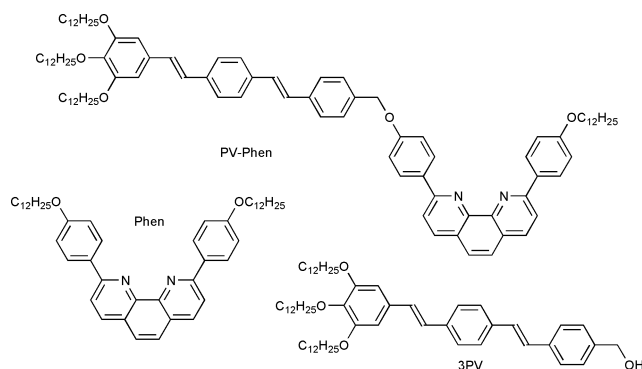
Interestingly, 3PV-Phen can act as a proton triggered molecular switch. Effectively, the intense fluorescence of the 3PV-type moiety can be quenched (*off* state) by protonation of the phenanthroline unit upon addition of acid, whereas the starting emission can be restored (*on* state) by adding a base. The functioning of the 3PV-Phen switch is schematically represented in Fig. 1.

The synthesis of 3PV-Phen is depicted in Scheme 1. Treatment of *p*-bromododecyloxyphenyl with Bu^{t}Li in THF at −78 °C followed by quenching with 1,10-phenanthroline, hydrolysis and oxidation with MnO_2 gave **1** (85% yield). Reaction of **1** with *p*-lithio[(*tert*-butyldimethylsilyl)oxy]-phenyl[9] followed by hydrolysis and oxidation (MnO_2) yielded **2**
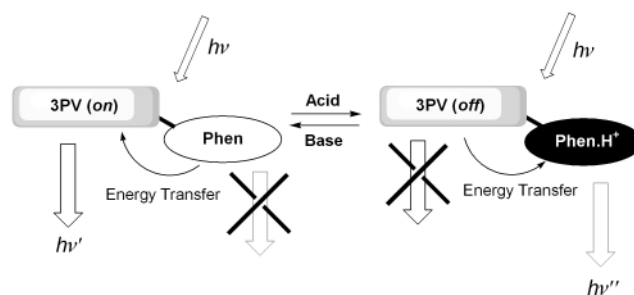

Fig. 1 Schematic representation showing the functioning of the 3PV-Phen molecular switch.

which after deprotection (TBAF) gave **3** in an overall yield of 33%. The reaction of **3** with 3PV under Mitsunobu conditions afforded 3PV-Phen in 71% yield. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.

The electronic absorption and emission properties of the model compounds 3PV and Phen [Fig. 2(a)] are very similar to those of previously investigated OPVs[7] and substituted phenanthrolines.[10] Both molecules are strongly fluorescent in the VIS spectral region; 3PV exhibits a band with $\lambda_{max} = 460$ nm, $\tau = 1.3$ ns and $\Phi_{fl} = 0.77$, whereas Phen displays $\lambda_{max} = 398$ nm, $\tau = 2.1$ ns and $\Phi_{fl} = 0.35$.†

Addition of increasing amounts of trifluoroacetic acid (TFA) to a 1.5×10^{-5} M solution of Phen causes dramatic changes in the absorption spectrum, that are leveled off at *ca.* 10 equivalents of acid added. Isosbestic points are maintained at 296, 314 and 356 nm indicating that a single chemical process occurs, *i.e.* protonation of the phenanthroline;[10] interestingly, the initially transparent solution becomes yellow at the end of the titration. In parallel with the changes in the absorption spectra, remarkable variation in the fluorescence properties are recorded. The intense luminescence band of Phen progressively disappears while a new band characteristic of PhenH$^+$ grows at
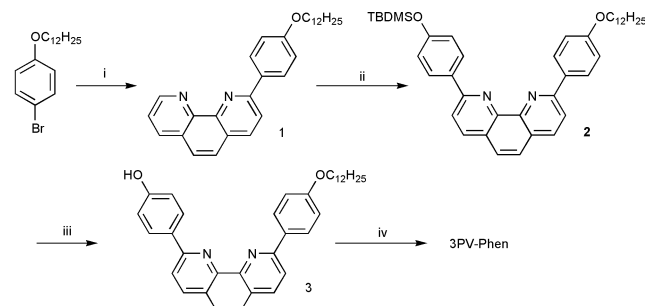
Scheme 1 *Reagents and conditions*: i, Bu^{t}Li, THF, −78 °C, 1 h, then 1,10-phenanthroline, −78 to 0 °C, 3 h, then H_2O, then MnO_2, room temp., 1 h; ii, *p*-lithio[(*tert*-butyldimethylsilyl)oxy]phenyl, THF, 0 °C, 4 h, then H_2O, then MnO_2, room temp., 1 h; iii, TBAF, THF, 0 °C, 2 h; iv, 3PV, DEAD, PPh$_3$, THF, reflux, 72 h.
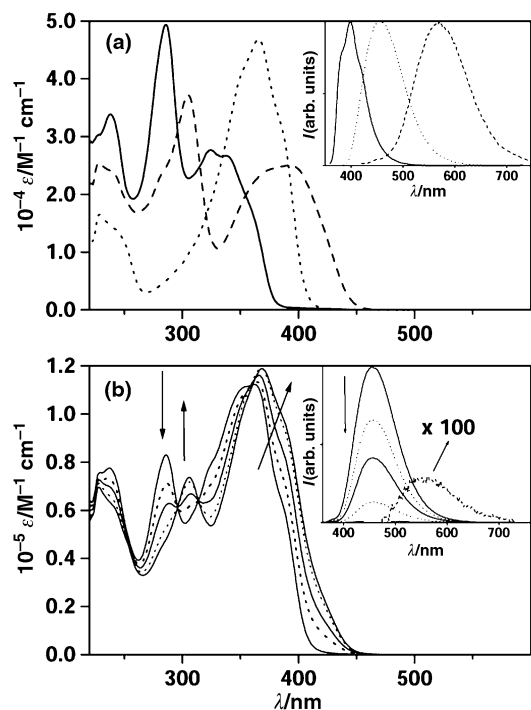
Fig. 2 (a) Absorption and (inset) fluorescence spectra of 3PV (······), Phen (——), and PhenH⁺ (– – –). (b) Absorption and (inset) fluorescence (λ_{exc} = 314 nm, isosbestic point) spectra of a 1.5×10^{-5} M CH$_2$Cl$_2$ solution of 3PV-Phen containing 0, 1, 2, 4 or 20 equivalents of trifluoroacetic acid. The weak red-shifted band is obtained for the solution containing 20 equiv., after subtraction of the residual 3PV luminescence (see text).

570 nm, with τ = 12.2 ns and Φ_{fl} = 0.048; the luminescence color switches from purple (Phen) to yellow (PhenH⁺). Addition of an organic base [diazabicyclo[4.3.0]non-5-ene (DBN)] restores the initial absorption and luminescence properties. Importantly, no changes of such properties are observed upon addition of a large excess of TFA or DBN to 3PV solutions.

The absorption spectrum of 3PV-Phen matches the sum of the spectra of the reference compounds within ±10% error, showing one diagnostic band for each component unit with maxima at 286 (Phen) and 360 nm (3PV). Only the typical fluorescence band of the 3PV fragment is observed (λ_{max} = 460 nm, τ = 1.3 ns, Φ_{fl} = 0.70); the excitation spectrum (λ_{em} = 460 nm) matches the absorption profile, indicating that excitation of the Phen moiety is followed by quantitative energy transfer to the 3PV unit. One can thus conclude that, in 3PV-Phen, only the OPV luminescence is *on* since a photoinduced quenching process featuring a Phen → 3PV direction is active (Fig. 1).

Addition of increasing amounts of (TFA) to a 1.5×10^{-5} M solution of 3PV-Phen causes dramatic changes in the absorption spectrum [Fig. 2(b)]. A clear analogy with the protonation reaction of Phen is found: the same amount of acid is required to complete the reaction, isosbestic points are located at 296, 314 and 359 nm. Importantly, the final spectrum matches the sum of the spectra of 3PV and Phen.H⁺ within ±10% error, and the reaction is reversible upon addition of DBN. These findings suggest that the 3PV-PhenH⁺ species is formed.

The addition of acid also leads to dramatic changes in the emission properties (λ_{exc} = 359 nm, isosbestic point): the characteristic blue 3PV luminescence is progressively suppressed and a much weaker green-yellow emission (λ_{max} = 556 nm, τ = 12.7 ns‡) is detected, attributable to the PhenH⁺ moiety (see above). The luminescence quenching of 3PV, observed also in a rigid matrix at 77 K, is attributable to energy transfer to the PhenH⁺ moiety. The energy transfer efficiency is difficult to estimate, since some residual 3PV fluorescence (<0.5%, relative to the initial value) is present, even when a large excess of acid is added. Such residual emission, likely arising from unprotonated 3PV-Phen in the acid–base equilibrium, overlaps the much weaker PhenH⁺ emission, thus making difficult clean excitation spectroscopy. In any case one can conclude that, in an acid environment, the OPV luminescence of 3PV-Phen is *off* due to an intercomponent quenching process displaying a 3PV → Phen direction [Fig. 1].

In terms of electronic energy levels our bipartite system has been designed in order to achieve the following: in one component (3PV) the energy of the fluorescent level (E_1) is insensitive to protons; by contrast, in the other component (Phen), a proton input tunes the fluorescent levels between two energy values (E_2 and E_3). The key feature is that the energy of E_1 is intermediate between that of E_2 and E_3, thus enabling an energy transfer in the desired direction *via* the chemical (proton) input. The energy scaling ($E_2 > E_1 > E_3$) is reflected in the spectral position of the corresponding fluorescence bands [Fig. 2(a), inset].

In conclusion, we have shown a simple way to reversibly switch *on* and *off* the widely exploited fluorescence of OPVs. Also, it is worth pointing out that this is one of the rare cases of multicomponent systems where the direction of the photo-induced energy transfer can be controlled.[11–12] To the best of our knowledge, this is the first example where such control can be reversibly accomplished by chemical inputs.

Notes and references

† Fluorescence spectra, lifetimes (time resolution 0.5 ns), and quantum yields were obtained as described in detail in ref. 7; experimental uncertainties are ±2 nm, ±8% and ±20%, respectively. For emission quantum yields anthracene in cyclohexane (Φ = 0.34) and quinine sulfate in 0.05 M H$_2$SO$_4$ (Φ = 0.546) were used as standards.
‡ In this case the decay is biexponential and 12.6 ns refers to the longest component. A shorter component (1.3 ns) accounts for the residual 3PV fluorescence (see text).

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