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Synthesis and Spectral Characterization of Photoswitchable Oligo(p-phenylenevinylene)-Spiropyran Dyad

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Abstract: In view to design new class of photoswitchable fluorescence probes and operate them to solution as well as onto solid substrate we have envisioned the possibilities of attaching photochromic spiropyran (SP) to highly efficient fluorophore Oligo(p-phenylenevinylene) (OPV). A new dyad SP-OPV-SP(10) was synthesized and characterised both in solution as well as film onto solid substrate where two SP units as photochromic acceptors are attached to the two ends of OPV, a fluorescent donor. External stimulations (ultraviolet light, visible light and acid) generate reversible changes of the structure resulting the changes of absorption spectrum and fluorescence emission spectra of dyad 10 due to the presence of two spiropyran units. Photoinduced (ultraviolet light) isomerization of the spiropyran causes 60% decrease in the emission intensity of the OPV at the photostationary state in solution of 60 µM concentration. In solid state, ultraviolet irradiation causes ~98% reduction of fluorescence intensity of OPV. The photogenerated isomer is quite more stable in solid state than that in solution. The fluorescence intensity of dyad 10 is modulated by reversible conversion among the three states of the photochromic spiropyran units and the fluorescence resonance energy transfer (FRET) between the MC form of SP and the OPV unit. In any case, these investigations demonstrate that design of dyad 10 is viable for the realization of photoswitchable molecular assemblies and can evolve as efficient fluorescent probes for potential applications towards molecular device design like integrated logic gate with multiple inputs and single output.

Introduction

Materials with properties that can be modulated by external inputs, such as optical excitation, thermal excitation and chemical stimulation, are of high interest in a broad range of potential applications in advanced molecular optical devices. Fluorescence spectroscopy has become a very sensitive diagnostic tool both in bulk and single molecule level. It is rapidly growing as an important methodology in many biological diagnosis, imaging, detection applications and in different molecular device applications which include fluorescence switch, fluorescence sensor and other photonic devices, primarily because of its ease of use. Furthermore, the modulation of fluorescence emission properties of fluorescent dye molecule is being explored in biological studies to selectively highlight cells, organelles or proteins. Hence, control or reversible modulation of fluorescence properties of dye molecules is a fascinating field of studies. In this context, photochemical isomerisation, a light-driven transformation of a photochromic compound, between two isomeric forms could lead process where the two forms may have their own spectroscopic identity with different absorption and emission spectra. Because of the difference in electron distribution in two isomers, their physical and chemical properties may differ in many ways, such as refractive index, dielectric constant, redox potential, chelation potential, absorption spectrum, fluorescence properties, and so on, and make them suitable for different practical applications. When such photochromic compounds are attached to a fluorophore, their properties can be tuned by selective photoirradiation. Among them, 1,3-dihydro-1,3,3-trimethyl-spiro[2H-1-benzopyran-2, 2-(2H)-indole] which is popularly known as spiropyran (SP) has been extensively investigated for different fluorophores exploiting light driven reversible interconversion between two states, close ring SP and open ring merocyanine (MC). In addition to this, protonated form of MC can provide another state (MCH) which has different characteristic absorption properties than that of MC and it is reversibly interconverted between MCH and SP by alternate acid-base titration. To achieve photoreversible fluorescence modulation of any fluorophore, one needs to allow photoinduced electron transfer or fluorescence resonance energy transfer (FRET) to occur to quench the excited states of fluorophore. The basic requirement of FRET is the specific fluorophore must be covalently linked to the spiropyran molecule (or linked to it through a spacer) and the certain degree of spectral overlap between the emission spectrum of the fluorophore (donor)
and the absorption spectrum of the acceptor. The three states of spiropyran SP, MC, and MCH show quite different absorption spectra, and thus it is possible to regulate the fluorescence intensity of a suitable fluorophore by irradiation of the solution containing both spiropyran and fluorescent molecule. Indeed, Raymo and his colleagues studied the “signal communication” between pyrene (naphthalene, anthracene, and tetracene) and spiropyran, and proposed the corresponding integrated logic gates and communication network. By attaching spiropyran covalently to porphyrin, Moore et al. studied the quenching process of the porphyrin excited states upon irradiation by ultraviolet light.

Oligo(p-phenylenevinylene) (OPVs) is the most widely used fluorophore due to its high extinction coefficient, high fluorescence quantum yield, and the fact that its excitation wavelength lies in the visible-wavelength range. OPVs known to be efficient energy donors to different acceptors. The research groups of Meijer, Janssen and Würthner have extensively studied the energy transfer processes in quadruple H-bonded OPV self-assemblies and OPV-perylene bisimide coassemblies. This property of self-assembled OPVs makes them ideal energy donor scaffolds to suitable acceptors that facilitate FRET processes. Organogels based on OPVs with functional groups have been the target of increasing attention because of various potential applications as soft materials. Although, some SP-functionalized macromolecular gels have also been reported, to the best of our knowledge, OPVs with the SP moiety still remain rare.

OPV shows the emission in the range of 420-650 nm and MC, a photo-driven transformed state of SP, shows an additional absorption band in the range of 500-650 nm. Hence, the overlap between the fluorescence spectrum of OPV and the absorption spectrum of MC is significantly large. By contrast, there is almost no overlap between the fluorescence spectrum of OPV and the absorption spectra of SP and MCH. As a result, for the OPV-spiropyran system corresponding fluorescence “on/off” ratio can be well enhanced. Furthermore, OPV shows strong absorption above 400 nm, at which SP, MC, and MCH have very weak absorption. Thus, excitation of OPV at 415 nm will not perturb any of the three states of spiropyran (SP, MC, and MCH). Keeping this view in mind, we have attempted to explore the studies of the photoswitching behaviour of SP units in the presence of the OPV unit.

Here we report the synthesis and spectral studies of as prepared dyad in solution as well as in cast film. The ease of synthesis allows us to covalently attach two SP units to the both side of an OPV unit making dyad (see Scheme 1-3). Demonstrated results confirm that the fluorescence intensity of the OPV unit can be regulated by alternate application of ultraviolet light, visible light, and acid-base titration. Hence, this SP-OPV-SP dyad can potentially be used in molecular device design at the single molecular level in view of processing and communicating information. In order to compare the intermolecular communicating behaviour of the mixture solution of an OPV derivative (compound 7, see Scheme 1) and a SP molecule (reference compound 11, see Scheme 2) (in a molar ratio of 2:1) were also investigated.

**Experimental**

**Materials and Instrumentation**

The solvents and the reagents were purified and dried by usual methods prior to use. Dodecyl bromide, triphenyl phosphine, LiAlH4 and NaBH4 were purchased from Sigma-Aldrich. Paraformaldehyde, HBr in acetic acid, NaH, NaOH, potassium acetate, hydroquinone and PCC were used as received from commercial suppliers. 1H NMR was recorded on 500 MHz (Bruker ARX500) and 13C NMR spectra were recorded on Bruker 300 MHz spectrometer at room temperature in CDCl3. The chemical shifts are reported in ppm (d) tetramethylsilane (TMS) as internal standard and coupling constant (J) are expressed in Hz. FT-IR spectra were recorded on a Shimadzu IRPrestige-21 Fourier Transform Infrared Spectrophotometer. MALDI-TOF mass spectrometry was conducted on a Perspective Bio systems Voyager- DE PRO mass spectrometer using a-Cyano-4-hydroxy cinnamic acid (CHCA) as the matrix and ESI- PerkinElmer Sciex, API 3000 mass spectrometer. Reactions were monitored by thin-layer chromatography (TLC) using 0.20-0.25 mm silica gel plates. Column chromatography was performed with silica gel (60-120 and 100-200 mesh). All UV/vis spectra were recorded using Hitachi U-2910 spectrophotometer. All steady state fluorescence spectra were recorded at room temperature by Fluorolog-3 spectrofluorimeter of Horiba Jobin Yvon, USA.

**Synthesis of OPV**

**1,4-Bis(dodecyloxy)benzene (1):** A suspension of 1,4-hydroquinone (5 g, 45 mmol), 1-bromododecane (32.4 mL, 135 mmol), and K2CO3 (18.7 g, 135 mmol) in Acetonitrile (200 mL) was heated at reflux for two days before being poured into water (400 mL). The precipitates were first collected by filtration and then dissolved in a minimum of hot hexane. Subsequently, the resulting hot solution was poured into methanol (200 mL) to precipitate the product. The precipitates were filtered off and dissolved in hot hexane (100 mL) again. Reprecipitation of resulting solution in methanol then gave 17.0 g pure product 1 as a white solid, after filtered and dried under vacuum (85%). 1H NMR (CDCl3) δ (ppm) 0.87 (m, 6H, CH3), 1.24-1.85 (m, 40H, CH2), 3.85 (t, J = 6.40 Hz, 4H, OCH2), 6.82 (s, 4H, aromatic).

**2,5-Bis(bromomethyl)-1,4-bis(dodecylxy)benzene (2):** To a suspension of 1 (2.28 g, 5.2 mmol) and paraformaldehyde (0.33 g, 11.0 mmol) in acetic acid (25 mL) was added HBr (2.2 mL, 31 wt % in acetic acid) all at once. This mixture was then heated to 60-70°C with stirring for 2 h. As the reaction proceeded, the suspension changed to clear solution first and then became a thick suspension. After cooling to room temperature, this suspension was poured into water (150 mL). The precipitates were filtered and dissolved in hot chloroform. Reprecipitation of resulting solution in methanol then gave 2...
**Scheme 1:** Synthetic route of OPV (a) Bromododecane, K$_2$CO$_3$, Acetonitrile, reflux, 36 h, 85%; (b) paraformaldehyde, HBr, 60 °C, 2 h, 86%; (c) KOAc, Bu$_4$NBr, Acetonitrile, reflux, overnight, 100%; (d) LiAlH$_4$, THF, room temperature, 2 h, 99%; (e) PCC, CH$_2$Cl$_2$, room temperature, 2 h, 87%; (f) PPh$_3$, toluene, reflux, 3 h; (g) (i) 5, LiOEt, CH$_2$Cl$_2$, room temperature, 10 min; (ii) I$_2$, CH$_2$Cl$_2$, room temperature, overnight, 84%. (h) NaBH$_4$, CH$_3$OH, CH$_2$Cl$_2$, room temperature, 45 min.

(2.83 g, 86.1% yield) as a white, loose solid after being filtered and dried under vacuum. $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 0.87 (m, 6H, CH$_3$), 1.24-1.85 (m, 40H, CH$_2$), 3.98 (t, $J = 6.42$ Hz, 4H, OC$_2$H$_2$), 4.52 (s, 4H, CH$_2$Br), 6.85 (s, 2H, aromatic).

2,5-Bis(acetyl methyl)-1,4-bis(dodecyloxy)benzene (3): A solution of 2 (2.2 g, 3.4 mmol), potassium acetate (1.03 g, 10.4 mmol), and tetra n-butyl ammonium bromide (0.17 g) in a mixture of Acetonitrile (50 mL) and chloroform (25 mL) was heated at reflux overnight. The resulting mixture was poured in water (50 mL) and extracted with chloroform (3x50 mL). The extracts were washed with water (2x50 mL). Solvent from the resultant organic solution was removed on a rotary evaporator after drying over anhydrous sodium sulphate. This furnished product 3 (2.0 g, 100% yield). $^1$H NMR (CDCl$_3$) $\delta$ (ppm) 0.87 (m,
was separated, washed with water, and dried over anhydrous sodium sulphate. The residues, after removal of solvents, contained both E- and Z-isomers. A solution of this isomer mixture and iodine (500 mg) in methylene chloride (50 mL) was stirred at room temperature for overnight. The dark brown solution was then diluted with methylene chloride and washed consecutively with aqueous Na₂S₂O₃ solution (1.0 M, 2×75 mL) and water. After being concentrated on a rotary evaporator, this solution was loaded onto a silica gel column and eluted with a mixture of hexane and chloroform (1:1 v/v). This afforded 1.21 g (83.9%) of compound 6 as a yellow fluorescent solid. ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 18H, CH₃), 1.24–1.83 (m, 40H, CH₂), 3.97 (t, J = 6.31 Hz, 4H, OCH₂), 4.67 (s, 4H, CH₂OH), 6.92 (s, 2H, aromatic). ¹³C NMR (CDCl₃) δ (ppm) 124.9–126.1 (s, 12H, aromatic), 10.52 (s, 2H, CHO).

2,5-Bis(2,5-didodecyloxy-4-formyl)phenylenevinylene]-benzene (7): The bis-aldehyde 6 (0.29 g, 0.2 mmol) was dissolved in a mixture of methanol (10 mL) and dichloromethane (25 mL). To this, sodium borohydride (15 mg, 0.4 mmol) was added and stirred at room temperature for 45 minutes. The reaction mixture was poured into water and extracted with dichloromethane. The organic layer was concentrated to give the corresponding alcohols. This afforded 0.25 g (87%) of compound 7 as a yellow fluorescent solid. ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 18H, CH₃), 1.25–1.83 (m, 40H, CH₂), 2.4 (s, 2H, OH), 3.9–4.0 (m, 12H, OCH₂), 4.67–4.69 (s, 4H, CH₂), 4.02–4.12 (m, 4H, CH₂OH), 6.86 (s, 2H, aromatic), 7.20 (s, 2H, aromatic H₃,H₃'), 7.33 (s, 2H, aromatic H₂,H₂'), 7.49 (d, 2H, J = 16.56 Hz, vinyl-H), 7.58 (d, 2H, J = 16.53 Hz, vinyl-H), 10.45 (s, 2H, CHO).

2,5-Bis(dodecylol)-1,4-bis[(2,5-didodecyloxy-4-hydroxymethyl)phenylenevinylene]-benzene (8): A mixture of 2,3,3-Trimethylindolenine (2.5 g, 15.7 mmol) and 3-iodopropanoic acid (3.14 g, 15.7 mmol) were dissolved in toluene was heated at reflux for 3 h. The solvent under reduced pressure on a rotary evaporator, this solution was loaded onto a silica gel column and eluted with a mixture of hexane and chloroform (1:1 v/v). This afforded 1.21 g (83.9%) of compound 6 as a yellow fluorescent solid. ¹H NMR (CDCl₃) δ (ppm) 0.87 (m, 18H, CH₃), 1.24–1.83 (m, 40H, CH₂), 3.97 (t, J = 6.31 Hz, 4H, OCH₂), 4.67 (s, 4H, CH₂OH), 6.92 (s, 2H, aromatic).
resulting solution was evaporated; the remaining product dissolved in water (100 mL) and was washed with chloroform (50 mL) for 3 times. Evaporation of water gave product 8 (4.07 g, 72 %) as a red oil. 1H NMR (DMSO-d6, 400 MHz): δ 1.53 (s, 6H), δ 2.85 (s, 3H), δ 2.96-3.0 (t, 2H), δ 4.63-4.67 (t, 2H), δ 7.61-7.64 (m, 2H), δ 7.82-7.84 (dd, 1H), δ 7.97-8.0 (dd, 1H).

Synthesis of SP-OPV-SP (10)

Compound DCC (29 mg, 0.14 m mol) was added to a solution of 9 (180 mg, 0.47 mmol), methanol (1 mL, 25 mmol) and DMAP (3.8 mg, 0.03 mmol) in dry CH2Cl2 (100 mL) and temperature was initially maintained at 0°C under Ar. Then, the mixture was allowed to warm up to ambient temperature over 12 h and stirred for a further 12 h. Solvent was evaporated and the residue dissolved in chloroform. It was then precipitated by the addition of methanol and filtered. The crude mixture was then purified by column chromatography [SiO2: Hexane/CHCl3 (1:1 v/v) to afford 11 (130 mg, 70%). 1H NMR (500 MHz, CDCl3): δ 1.07 (s, 3H), δ 1.19 (s, 3H), δ 2.45-2.57 (t, 2H), δ 3.34-3.40 (t, 2H), δ 5.98-6.01 (d, 1H), δ 6.65-6.67 (d, 1H), δ 6.78-6.82 (t, 1H), δ 6.85-6.88 (d, 1H), δ 7.11-7.14 (t, 1H), δ 7.19-7.22 (d, 1H), δ 7.98-8.21 (dd, 1H), δ 8.21 (s, 1H).

Reference Compound SP (11): Compound DCC (97 mg, 0.47 mmol) was added to a solution of 9 (180 mg, 0.47 mmol), methanol (1 mL, 25 mmol) and DMAP (3.8 mg, 0.03 mmol) in dry CH2Cl2 (100 mL) and temperature was initially maintained at 0°C under Ar. Then, the mixture was allowed to warm up to ambient temperature over 12 h and stirred for a further 12 h. Solvent was evaporated and the residue dissolved in chloroform. It was then precipitated by the addition of methanol and filtered. The crude mixture was then purified by column chromatography [SiO2: Hexane/CHCl3 (1:1 v/v) to afford 11 (130 mg, 70%). 1H NMR (500 MHz, CDCl3): δ 1.07 (s, 3H), δ 1.19 (s, 3H), δ 2.45-2.57 (t, 2H), δ 3.34-3.40 (t, 2H), δ 3.7 (s, 3H), δ 5.98-6.01 (d, 1H), δ 6.65-6.67 (d, 1H), δ 6.78-6.82 (t, 1H), δ 6.85-6.88 (d, 1H), δ 7.11-7.14 (t, 1H), δ 7.19-7.22 (d, 1H), δ 7.98-8.21 (dd, 1H), δ 8.21 (s, 1H).

Results and Discussion

The synthesis of SP-functionalized OPV (10) is shown in Scheme 3. Compounds 7 and 9 were prepared according to the sequence shown in Scheme 1 and Scheme 2. Reaction of acid-alcohol coupling between 7 and 9 in the presence of DCC, DMAP led to SP-OPV-SP dyad (10) in 50% yield.

Absorption Spectra:

As prepared reference spiropyran compound SP (11) shows the typical reversible interconversion among the corresponding SP, MC, and MCH states upon irradiation of ultraviolet (350 nm) and visible light (580nm) and addition of acid (ESI, Figure 1S). Similar phenomena were observed for the mixed solution of reference compounds 11 and 7 (in a molar ratio of 2:1), but no change in absorption spectra of OPV (7) was observed.
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Figure 2. Normalized absorption spectra of SP-OPV-SP (10). (A) in ACN solution (~10⁻⁵ M) and (B) as a cast film onto quartz plate at room temperature. (a) black curve, before irradiation of UV light, (b) magenta curve, after irradiation of UV light (350 nm) and (c) orange curve, after irradiation of Vis light 580 nm and (d) blue curve, addition of 2 equivalent of CF₃COOH immediate after UV irradiation respectively. Inset in (A) show the enlarge view of absorbance in visible range.

Figure 3. Photograph of the cast film of 10 prepared from DCM solution (~10mM), (a) before 350 nm light irradiation (b) after 350 nm light irradiation for 10 seconds (c) after 570 nm light irradiation (d) after CF₃COOH vapour exposure.

In order to check the photoinduced reversible interconversion of 10 in solid state, we have prepared cast film of 10 from (~5mM) DCM solution onto quartz plate. The surface morphology of the cast film of 10 shows good network structure indicating the formation of gel (ESI, Figure 3S), like reference OPV (7)₁⁵. The absorption spectra of as prepared cast film of 10 was very similar to that observed in solution (Figure 2B) with a little red shift of OPV absorption peak. The colour of the film was greenish-yellow. However, as shown in Figure 3, the colour of the film turned to dark blue after the film was exposed to 350 nm (150 Xenon Lamp) light for just 10 seconds. Consequently, the absorption spectra of this film...
shows a prominent peak at 570 nm corresponding to the MC form of 10 (Curve b, Figure 2B). This dark blue colour film turned back towards original colour upon irradiation with 570 nm light for 10 minutes. It is important to mention here that unlike in solution the photogenerated isomer (MC form) of 10 in film reverts thermally very slowly and it takes more than ~120 minutes to complete the 80% conversion. However, this cycle of photoinduced reversible colour change was repeated several times without degrading the sample colour as well as optical density. Upon expose to CF$_3$COOH vapour the colour of the dark blue film of MC form of 10 turns to be yellow (Figure 3) and corresponding absorption spectra is almost identical to the absorption spectra of 10, (Curve d, Figure 2B).

Fluorescence Spectra:
To ascertain if there is any self quenching of fluorescence emission of dyad 10 we have performed concentration as well as excitation wavelength dependent emission studies of 10 in ACN solution but no self quenching was observed till 100 µM concentration (ESI, Figure 6S, 7S and 8S). Figure 4 shows the fluorescence spectra of the ACN solution (60 µM) of dyad 10 under different experimental conditions with excitation wavelength at 415 nm. Before exposing to ultraviolet light, dyad 10 showed a broad emission band in the range of 425-650 nm with the maximum around 460 nm (Curve a, Figure 4A). This fluorescence spectra is quite similar to that of fluorescence emission spectra of reference OPV (7) in terms of fluorescence intensity as well as fluorescence emission spectral structure. (ESI, Figure 4G). A red shift of emission maxima of dyad 10 is observed with respect to the emission peak of reference OPV (7) (ESI, Figure 4G). However, upon irradiation with ultraviolet light (350 nm) for 10 minutes, the intensity of the fluorescence band around 460 nm decreased to 60% to that of the initial solution (Curve b, Figure 4A) and a very weak new fluorescence band peaking at around 630-640 nm appeared. It is important to note that in ACN solution MC form of SP(11) shows fluorescence emission peaking at 650 nm(ESI, Figure 1S). Upon irradiation by ultraviolet light the SP moieties of dyad 10 transform to MC conformer resulting formation of MC-OPV-MC, (Scheme 5) which quenched the excited state of the OPV unit through fluorescence resonance energy transfer. Energy transfer from the excited OPV state to MC produced the excited MC state, which should show a new emission band at around 650nm. However, in the present case we do observe such new fluorescence band relating to the fluorescence of MC moiety of MC-OPV-MC but the intensity of this band is too low to be resolved with high fidelity. Furthermore, same ACN solution of MC-OPV-MC shows very week fluorescence emission above 600nm upon excitation on 580 nm, absorption peak of MC moiety in MC-OPV-MC. This week fluorescence of MC form of dyad 10 could be more advantageous in using this compound in fluorescence switching application with enhanced contrast of fluorescence between "on/off" modes. However, after irradiation to MC absorption peak by 580 nm light for 2 minutes, MC-OPV-MC completely changed to SP-OPV-SP form and fluorescence intensity rebuilt to its initial values without distortion of fluorescence band shape (curve c, Figure 4A). These fluorescence “on/off” states are repeated by alternate application of 530 and 570 nm light for several times without degrading the compound (Figure 4A). This result confirms the light driven transformation between two states of dyad 10 is fatigue resistance in solution phase. In order to explore the role of third state, protonated form of MC, to the fluorescence modulation we add 2 equivalent of CF$_3$COOH to the solution of dyad 10 immediately after UV light...
irradiation. After addition of acid the fluorescence intensity of the solution was restored to 70% to its initial value (curve d, Figure 4A) without any deformation of spectral shape. Hence, efficiency of fluorescence modulation in case of treatment with ultraviolet light irradiation followed by addition of acid is bit lower than the treatment with alternate UV/Vis light. The reason behind this reduction of fluorescence modulation can be of three folds: (a) the conversion of MC to MCH form is not complete and there may be equilibrium between MC and MCH, (b) MCH-OPV-MCH could show FRET and (c) MCH-OPV-MCH has higher non-radiative transition than SP-OPV-SP.

Since, the absorption spectra of MCH-OPV-MCH does not show any trace of absorption in the range of 500-650 nm (Figure 2A, Curve d), the first two reasons cannot be accounted for the reduction of fluorescence modulation by MCH form. Hence, it can safely be attributed that MCH-OPV-MCH has less fluorescence yield than SP-OPV-SP.

![Scheme 5. Reversible fluorescence switching cycle of dyad 10 under different external stimuli: Ultraviolet light (350nm), Visible light (580 nm) and acid](image)

Similar sets of experiment were performed for the mixtures of reference compounds SP (7) and OPV (11) (in a molar ratio of 2:1) in order to compare the difference between intra and inter molecular effect in fluorescence switching behaviour. Before ultraviolet light irradiation, the solution showed a broad and featureless emission band with the maximum around 420 nm. After irradiation of the solution at 350 nm for 15 min, the fluorescence intensity was reduced by about 13%, which should be due to the quenching of the excited state of the OPV (11) by the corresponding MC form generated from the SP (7) upon ultraviolet light irradiation. The fluorescence intensity of the solution returned to its initial value upon irradiation with visible light. Similarly, UV irradiation followed by addition of 2 equivalents CF$_3$COOH retained back the fluorescence intensity to its initial value. As compared to dyad SP-OPV-SP (10), the modulation of fluorescence intensity for the mixed solution of 7 and 11 is significantly less. As per Förster theory$^{36}$, the energy transfer efficiency is strongly dependent on the donor-acceptor distance. The donor and acceptor units in dyad SP-OPV-SP (10) are much closer to each other than those in the case of the mixed solution of 7 and 11 (intermolecular). Thus, the intermolecular energy transfer is not that effective as that for the intramolecular case.

Sequentially similar type of experiments were performed with as prepared cast film of dyad 10. As shown in Figure 4B, the fluorescence emission spectra of the film of 10 is red shifted by 60 nm than that in ACN solution with peaking at 520 nm (Curve a, Figure 4B). A weak fluorescence peak is also observed at 750 nm. Excluding this tail end band, the fluorescence spectra of dyad SP-OPV-SP (10) resembles the typical OPV fluorescence characteristic in film form$^{37}$ (see ESI Figure 4S). Hence, OPV moiety retains its identity in tact in SP-OPV-SP (10) dyad. In other word, attachment of SP moiety to OPV does not alter the physical properties of OPV. However, after irradiation with 350 nm light for just 10 seconds, the fluorescence intensity of OPV moiety of dyad 10 at around 520 nm quenched 99% of its initial value and a strong new band appeared peaking at 750 nm (Curve b, Figure 4B). This new fluorescence emission band strongly resemblance to the fluorescence emission spectra of MC form of SP (11) in solid state as a film. (ESI Figure 2S). This result confirms efficient FRET between OPV and MC moieties. It is also important to note here, the weak appearance of this 750 nm band even before UV irradiation to the SP-OPV-SP film suggests that 415 nm excitation (for collection of fluorescence emission) converts some SP moieties of SP-OPV-SP to MC form. To check the photo-reversibility the film was irradiation by 570 nm light for 10 minutes and the fluorescence of OPV moiety came back to 30% of its initial value whereas fluorescence corresponding to MC moiety disappeared completely (Curve c, Figure 4B). This cycle is repeated several times and no remarkable degradation of compound was observed (Figure 4B). At this point, it is not clear why fluorescence of OPV moiety did not retain its initial value after first cycle of 570 nm irradiation whereas fluorescence of MC moiety vanished totally. To resolve this issue a systematic studies with different parameters of film preparation are essential and it is planned soon. However, after exposure of film to CF$_3$COOH vapour just after UV irradiation, the OPV fluorescence intensity was restored to 30% of its initial value along with concomitant decrease of MC fluorescence at around 750 nm (Curve d, Figure 4B). It is important to mention here that, the film of 10 was removed from the fluorometer and replaced back after having CF$_3$COOH vapour exposure to the film. In the process, the excitation was not performed exactly at the same area as before to monitor the fluorescence. Since, thickness of the cast film was not precisely uniform, quantitative analysis of fluorescence intensity was hampered. Moreover, the top surface of the film is exposed to acid vapour while bottom surface may not be exposed to acid vapour properly. As a results the colour of the acid vapour exposed film is not exactly same to that unexposed one (Figure 3). However, qualitatively it can be assured that the film of dyad 10 onto quartz plate attained three states of SP moiety upon alternate application of UV, Vis and acid respectively. Furthermore, for above all the studies, observed results are qualitative in nature and the quantitative
estimation were not performed. During the collection of fluorescence spectra, irradiation was not carried out. Hence, thermal reversion to the SP form could occur before and during the collection of fluorescence spectra, especially in solution where conversion of MC to SP form is very fast. Finally, since SP, MC and OPV absorb at 350 nm, irradiation at this wavelength creates only photostationary equilibrium between two forms (SP and MC) of spiropyran units, rather than complete conversion of the system to one form.

The above fluorescence modulation both in solution and film observed for dyad SP-OPV-SP (10) can be rationalized with the switching cycles starting and ending with SP-OPV-SP (10) as shown in Scheme 5. There should exist several states of dyad SP-OPV-SP (10) due to the partial conversion between SP and MC or vice versa on exposure to ultraviolet or visible light. Since changes of the fluorescence intensity are the sole parameter to account the conversion due to irradiation with UV/Vis light, we consider three ultimate states (Scheme 5) to clarify the mechanism. Upon irradiation with ultraviolet light, the SP moieties in dyad 10 are transformed to MC moieties forming to MC-OPV-MC, which quenches the excited state of the OPV moiety and the fluorescence intensity of the OPV moiety is reduced to about 50-60% of the initial value. An addition of 2 equiv of CF$_3$COOH (in solution), the MC moieties are converted to the MCH moiety and formed MCH-OPV-MCH, whose absorption spectrum is almost similar to SP-OPV-SP (10) and has no overlap with the fluorescence spectrum of the OPV moiety, a requirement of FRET process to occur. Thus, no energy transfer is occurred and the fluorescence intensity of the OPV moiety returns. On the other hand, upon irradiation of the solution of MC-OPV-MC with visible light, the complete conversion from MC-OPV-MC to SP-OPV-SP occurs in solution and the fluorescence intensity returns to its initial value. Thus, alternate application of ultraviolet light, visible light, and acid regulates explicitly the fluorescence intensity of the OPV moiety. This external stimulations dependence fluorescence spectrum of 10 can be exploited to design the integrated logic circuit in molecular level.

Conclusion:

In summary, we have successfully synthesized new dyad SP-OPV-SP and characterized its spectral properties both in solution and solid state. The presence of SP units controls the fluorescence switching ‘on/off’ states of OPV moiety by way of reversible interconversion among the three different states of photochromic spiropyran moiety and fluorescence resonance energy transfer (FRET) between MC and OPV moieties. These results may have implications for the invention of efficient fluorescent probes for potential applications towards molecular device design like integrated logic gate with multiple inputs and single output.

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Notes and references


