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Synthesis and Spectral Characterization of Photoswitchable Oligo(p-phenylenevinylene)s -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)s (**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, ultraviolate 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.[1] Fluorescence spectroscopy has become a very sensitive diagnostic tool both in bulk and single molecule level[2]. It is rapidly growing as an important methodology in many biological diagnosis[3], imaging[4], detection applications[5] and in different molecular device applications which include fluorescence switch[6], fluorescence sensor[7] and other photonic devices[8], 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.[9] 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[10,11]. Among them, 1,3-dihydro-1,3,3- trimethyl-spiro[2*H*-1-benzopyran-2, 2-(2*H*)-indole] which is popularly known as spyropyran (**SP**) has been extensively investigated for different fluorophores exploiting light driven reversible interconversion between two states, close ring **SP** and open ring merocyanine (**MC**)[11]. 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**)[12] 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)

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[a] Electronic supplementary information (ESI) available: Uv/Vis Spectra, fluorescence spectra of reference compounds , SEM Image of cast film and relevant fluorescence spectral data along with ^{1}H NMR & ^{13}C NMR data.

and the absorption spectrum of the acceptor. The three states of spiropyran **SP**, **MC**, and **MCH**[13] 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[14] 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.[15] studied the quenching process of the porphyrin excited states upon irradiation by ultraviolet light.

Oligo(*p*-phenylenevinylene)s (**OPV**s) 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. **OPV**s known to be efficient energy donors to different acceptors.[16-23] The research groups of Meijer, Janssen and Würthner have extensively studied the energy transfer processes in quadruple H-bonded **OPV** self-assemblies[24,25] and **OPV**-perylene bisimide coassemblies.[26,27] This property of self-assembled **OPV**s make them ideal energy donor scaffolds to suitable acceptors that facilitate FRET processes.[28] Organogels based on **OPV**s with functional groups have been the target of increasing attention in recent years because of various potential applications as soft materials.[29] Although, some SP-functionalized macromolecular gels have also been reported[30], to the best of our knowledge, **OPV**s 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 explored 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 **(10)** 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 **SP-OPV-SP(10),** 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. ^{1}H NMR was recorded on 500 MHz (Bruker ARX500) and ^{13}C NMR spectra were recorded on Bruker 300 MHz spectrometer at room temperature in $CDCl_3$. 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 K_2CO_3 (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%). ^{1}H NMR ($CDCl_3$) δ(ppm) 0.87 (m, 6H, CH_3), 1.24- 1.85 (m, 40H, CH_2), 3.85 (t, *J* = 6.40 Hz, 4H, OCH_2), 6.82 (s, 4H, aromatic).

***2,5-Bis(bromomethyl)-1,4-bis(dodecyloxy)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**

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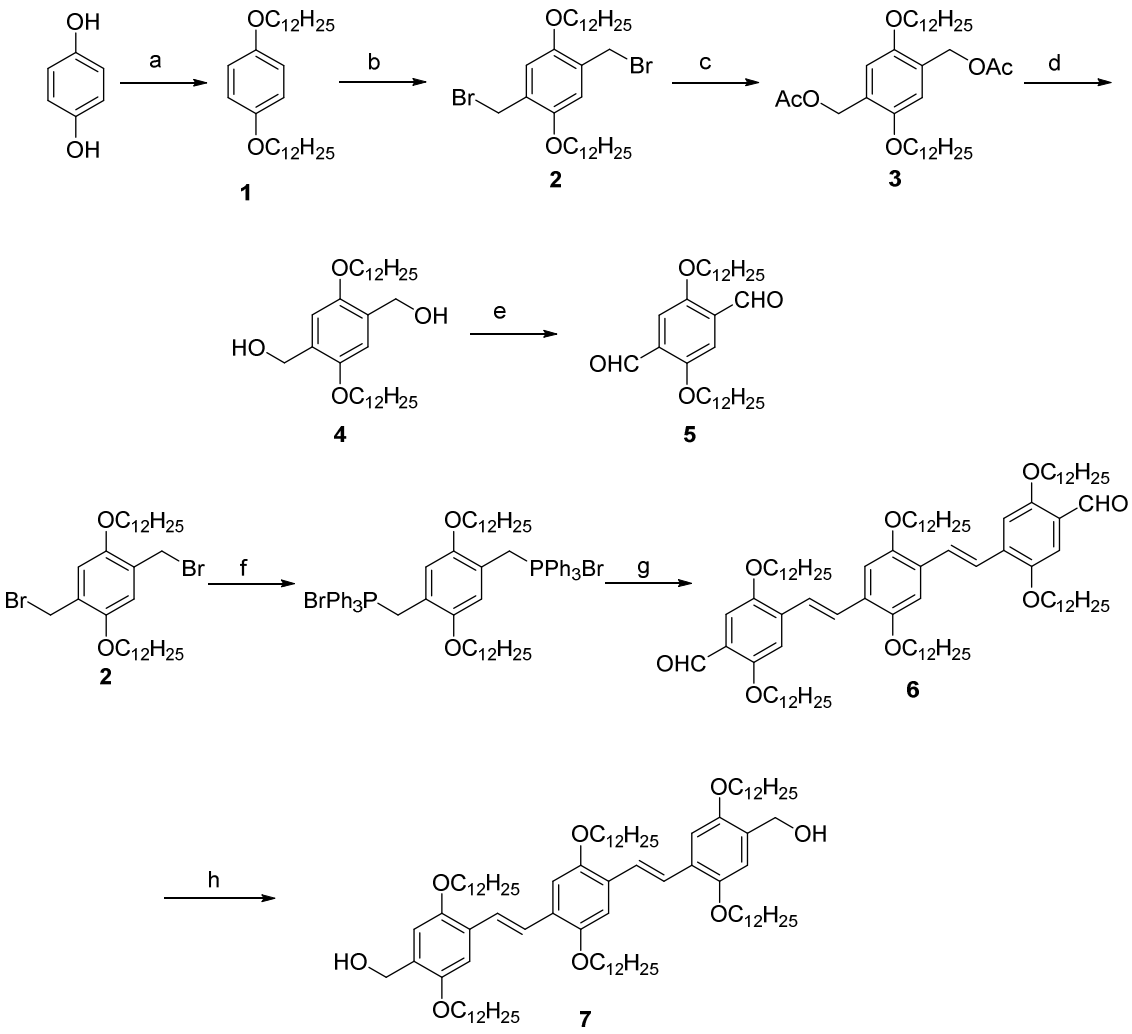
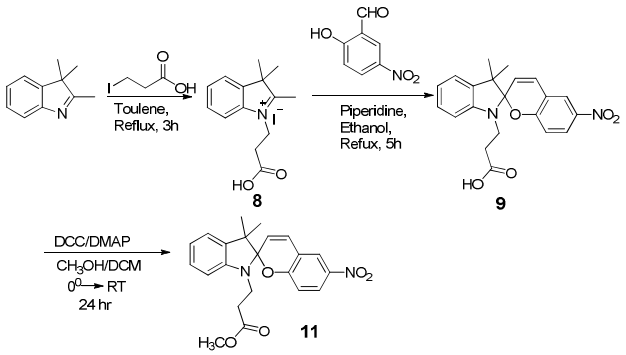


Scheme 1: Synthetic route of OPV (a) Bromododecane, K_2CO_3, Acetonitrile, reflux, 36 h, 85%; (b) paraformaldehyde, HBr, 60 °C, 2 h, 86%; (c) KOAc, Bu_4NBr, Acetonitrile, reflux, overnight, 100%; (d) $LiAlH_4$, THF, room temperature, 2 h, 99%; (e) PCC, CH_2Cl_2, room temperature, 2 h, 87%; (f) PPh_3, toluene, reflux, 3 h; (g) (i) 5, LiOEt, CH_2Cl_2, room temperature, 10 min; (ii) I_2, CH_2Cl_2, room temperature, overnight, 84%. (h) $NaBH_4$, CH_3OH, CH_2Cl_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 ($CDCl_3$) δ (ppm) 0.87 (m, 6H, CH_3), 1.24- 1.85 (m, 40H, CH_2), 3.98 (t, J = 6.42 Hz, 4H, OCH_2), 4.52 (s, 4H, CH_2Br), 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 (3×50 mL). The extracts were washed with water (2×50 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 ($CDCl_3$) δ (ppm) 0.87 (m,

6H, CH_3), 1.24- 2.06 (m, 46H, CH_2), 3.94 (t, *J* = 6.43 Hz, 4H, OCH_2), 5.14 (s, 4H, CH_2OAc), 6.88 (s, 2H, aromatic).



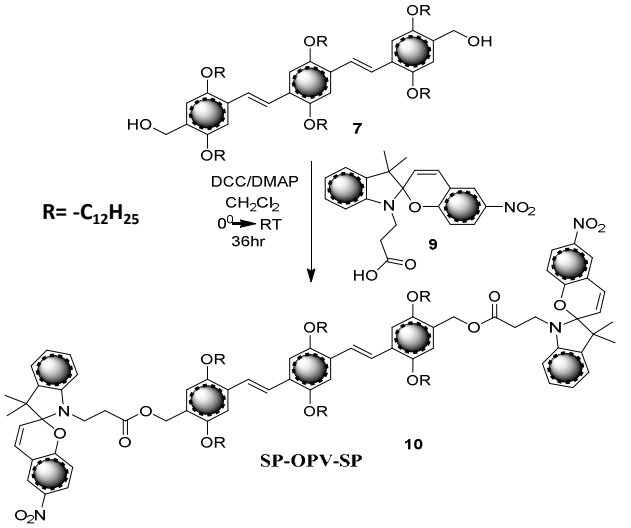
Scheme 2: Synthetic route of the carboxyl-containing spiropyran (SPCOOH) and reference spiropyran compound.

2,5-Bis(hydroxymethyl)-1,4-bis(dodecyloxy)benzene (4): To a suspension of $LiAlH_4$ (0.45 g, 11.2 mmol) in dry THF was added a solution of **3** (1.65 g, 2.8 mmol) in dry THF (50 mL) drop wise. The mixture was stirred at room temperature for 2 h. The excess of $LiAlH_4$ was quenched by addition of ethyl acetate at 0 °C. The resulting suspension was poured into water and followed by extraction with chloroform (75 mL). The extracts were combined and washed with water (100 mL). Removal of solvent under reduced pressure on a rotary evaporator furnished a white solid. It weighed **4** (1.4 g, 99.1% yield) after drying under vacuum. ^{1}H NMR ($CDCl_3$ + CD_3OD) δ (ppm) 0.87 (m, 6H, CH_3), 1.24- 1.85 (m, 40H, CH_2), 3.97 (t, *J* = 6.31 Hz, 4H, OCH_2), 4.67 (s, 4H, CH_2OH), 6.92 (s, 2H, aromatic).

***2,5-Bis(dodecyloxy)benzene-1,4-dialdehyde (5*)**: A suspension of **4** (1.4 g, 2.65 mmol) and pyridinium chlorochromate (PCC) (2.3 g, 10.6 mmol) in methylene chloride (100 mL) was stirred at room temperature for 2 h. The reaction mixture was then directly transferred onto the top of a short silica gel column. The highly fluorescent product **5** was then washed off the column with chloroform. Thus, compound **5** was obtained in 85.8% (1.14 g). ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (m, 6H, CH_3), 1.24- 1.85 (m, 40H, CH_2), 4.08 (t, *J* = 6.60 Hz, 4H, OCH_2), 7.43 (s, 2H, aromatic), 10.52 (s, 2H, C*H*O).

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didecoxy-4-formyl)phenylenevinylene] benzene (6). A suspension of **2** (0.63 g, 1.0 mmol) and triphenylphosphine (0.55 g, 2.1 mmol) in toluene was heated at reflux for 3 h. The solvent was then removed from the resulting clear solution under reduced pressure. The resulting residue, along with dialdehyde **5** (1.0 g, 2.0 mmol), was dissolved in methylene chloride (50 mL). Lithium ethoxide solution (2.5 mL, 1.0 M in ethanol) was added to this solution drop wise via a syringe at room temperature. The base should be introduced at such a rate that the transient red-purple colour produced upon the addition of base should not persist. The resulting solution was allowed to stir for 10 min more after the completion of base addition. This solution was then poured into a dilute aqueous HCl. The organic layer 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 $Na_2S_2O_3$ 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. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (m, 18H, CH_3), 1.24- 1.85 (m, 120H, CH_2), 4.02-4.12 (m, 12H, OCH_2), 7.15 (s, 2H, central phenyl-*H*), 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, C*H*O).

2,5-Bis(dodecyloxy)-1,4-bis[(2,5-didodecyloxy-4-hydroxymethyl)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**[31] as a yellow fluorescent solid. ^{1}H NMR ($CDCl_3$) δ (ppm) 0.87 (m, 18H, CH3), 1.25- 1.83 (m, 120H, CH2), 2.4 (s, 2H, OH), 3.9-4.0 (m, 12H, OCH_2), 4.67-4.69 (s, 4H, CH_2OH), 6.86 (s, 2H, aromatic), 7.12 (s, 2H, aromatic), 7.14 (s, 4H, aromatic), 7.40- 7.45 (d, J=16.45, 2H, vinylic), 7.46-7.51 (d, J= 16.39, 2H, vinylic).

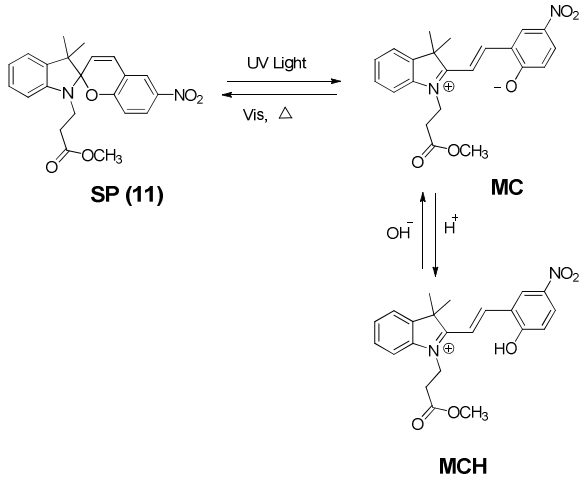


Scheme 3: Synthetic route of SP-OPV-SP from SPCOOH and OPV.

Synthesis of SP

1-(β-carboxyethyl)-2,3,3-trimethylindolenine iodide (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 (5 mL) and heated under nitrogen at 100°C for 3 h. The

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. ^{1}H NMR (DMSO-d_6, 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), δ7.97- 8.0(dd, 1H).



Scheme 4. Three switching states of references **SP** (**11**) compound.

***l-(β-carboxyethyl)-3',3'-dimethyl-6 -nitrospiro (indoline-2',2 [2H-1] benzopyran) (9*)**: The product **8** (2.52 g, 7 mmol), 5-nitrosalicylaldehyde (1.16 g, 7 mmol), and piperidine (0.76 mL, 0.7 mmol) were dissolved in anhydrous ethanol (50 mL). The mixture was refluxed for 5 h. The resultant dark purple mixture was cooled in an ice bath and filtered, and the filter cake was washed with cold ethanol. The precipitate was recrystallized from ethanol and dried in vacuum to yield **9**[32] (1.71 g, 65 %). ^{1}H NMR (DMSO-d_6, 400 MHz): 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), δ7.98- 8.21 (dd, 1H), δ 8.21 (s, 1H).

Synthesis of SP-OPV-SP (10)

Compound DCC (29 mg, 0.14 m mol) was added to a solution of **9** (35 mg, 0.09 mmol), **7** (202 mg, 0.14 mmol) and DMAP (2 mg, 0.01 mmol) in dry CH_2Cl_2 (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 24 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 [SiO_2: Hexane/$CHCl_3$ (1:1 v/v) to afford **10** (217 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02–7.95 (m, 4H), 7.45 (s, 4H), 7.2 –7.06 (m, 8H), 6.92–6.81 (m, 6H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.62 (d, *J* = 7.7 Hz, 2H), 5.82 (d, *J* = 10.3 Hz, 2H), 5.09 (s, 4H), 3.86–4.10 (m, 12H, OCH_2), 3.48-3.72 (m, 4H, CH_2N), 2.59-2.81 (m, 4H, CH_2CO), 1.09-1.91 (m, 132H, CH_2&CH_3), 0.79-0.91 (m, 18H, CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ 171.8, 159.4, 151.1, 150.4, 146.3, 141.0, 136.0, 128.3, 127.8, 127.3,127.0, 125.8, 123.2, 122.7, 121.9, 119.8, 118.6, 115.5, 115.1, 110.6, 109.5, 106.8, 69.6, 69.4, 62.0, 52.9, 39.4, 33.7, 33.4, 31.9, 29.7, 29.5, 29.4, 25.7, 22.7, 19.7, 14.1. FT-IR (KBr) vmax = 748, 806, 851, 963, 1022, 1089, 1123, 1206, 1269, 1339, 1383, 1421, 1485, 1509, 1579, 1610, 1737, 2852, 2924, 3057, 3447 cm-1.

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 CH_2Cl_2 (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 [SiO_2: Hexane/CHCl3 (1:1 v/v) to afford **11**[33] (130 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): 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), δ7.98- 8.21 (dd, 1H), δ 8.21 (s, 1H).

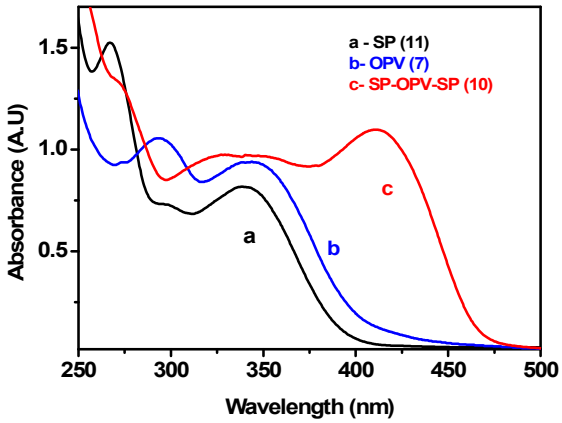


Figure 1. Absorption spectra of (a) **SP(11)**, (b) **OPV(7)** and (c) **SP-OPV-SP (10)** in ACN solution (~10^{-5} M) at room temperature.

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 spiropyrane 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)*[34]. 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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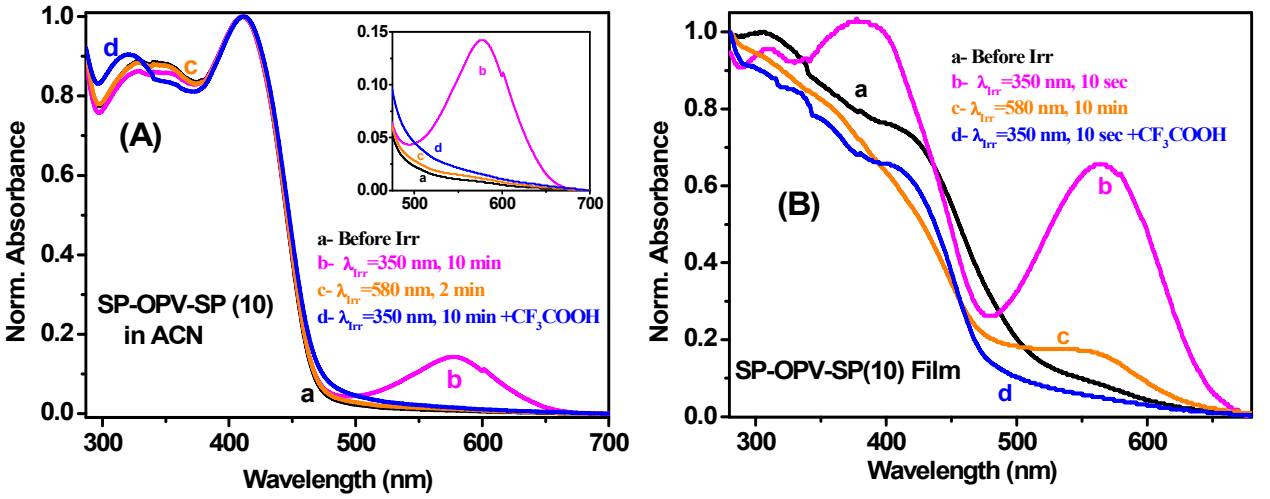


Figure 2. Normalized absorption spectra of **SP-OPV-SP** (**10**), (A) in ACN solution (~10^{-5} M) and (B) as a cast film onto quartz plate at room temperature. (a) black curve, before irradiation of UV light, (b) magenta curve, after irradiation of UV light (350 nm) and (c) orange curve, after irradiation of Vis light 580 nm and (d) blue curve, addition of 2 equivalent of CF_3COOH immediate after UV irradiation respectively. Inset in (A) show the enlarge view of absorbance in visible range.

Figure 1 shows the absorption spectrum of **OPV (7)** , **SP (11)** **SP-OPV-SP(10)** dyad in ACN**.** The absorption bands of **10** are essentially identical to those observed for **OPV** (7) and reference **SP** (**11**). Thus, the absorption spectrum of the dyad **SP-OPV-SP** is superposition of the spectra of the **OPV** and **SP** chromophores. However, a red shift of around 60 nm of **OPV** absorption peaking at 410 nm is observed in dyad **10** which can be due to enhance conjugation of **OPV** moiety after addition of **SP** unit. However, after the ACN solution of dyad **10** was irradiated with ultraviolet light at 350 nm (150W Xenon lamp) for 10 minutes, yellow greenish ACN solution of **10** turned to blue greenish solution. The characteristic absorption band of the **MC** form of **SP** with an absorption maximum at 580 nm emerged but the main absorption bands of the **OPV** unit remain unchanged (Figure 2A, Curve b). In comparison to the absorption spectrum of SP (11) upon ultraviolet light irradiation (*ESI Figure 1S*), it is confirmed that the formation of the corresponding **MC** form of **SP** in dyad **10** under the same conditions is occurred. This photogenerated isomer reverts to original one by two ways: (i) upon 580 nm irradiation for less than 2 minutes (ii) upon room temperature thermal isomerisation for ~5-6 minutes. Upon addition of 2 equivalent of CF_3COOH immediate after 350 nm light irradiation to the solution of **10**, the absorption band at 580 nm disappeared (Figure 2A, Curve c) due to the complete transformation of **MC** to **MCH** (Scheme 4).

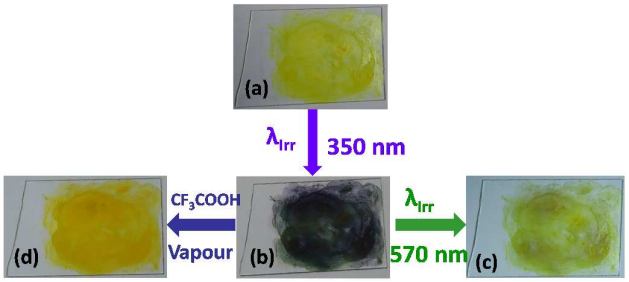


Figure 3. Photograph of the cast film of **10** prepared from DCM solution (~10mM), (a) before 350 nm light irradiation (b) after 350 nm light irradiation for 10 seconds (c) after 570 nm light irradiation (d) after CF_3COOH vapour exposure.

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**)[35]. 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_3COOH 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).

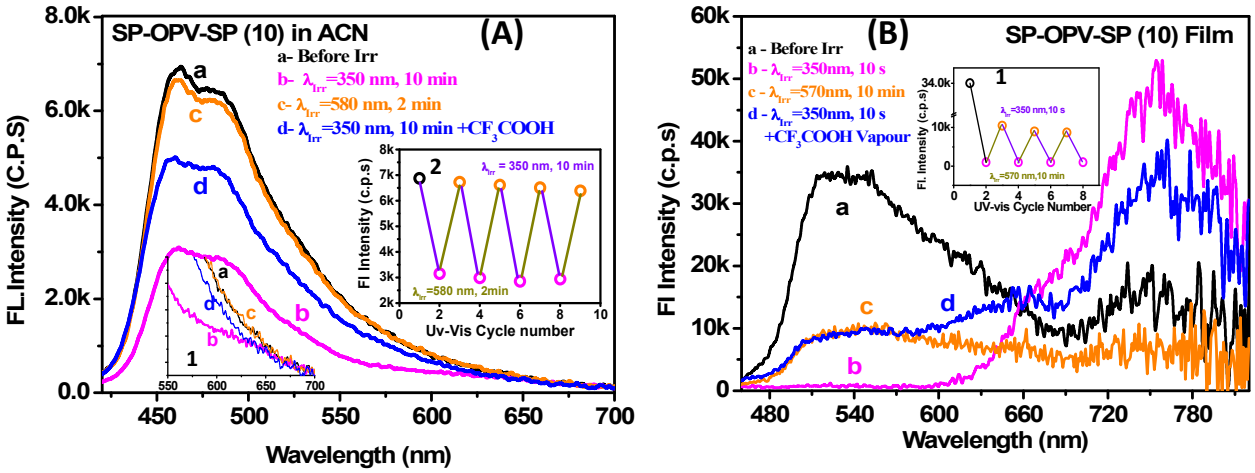


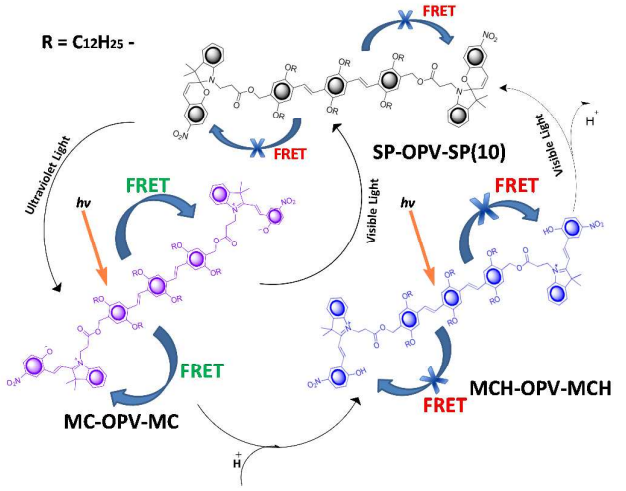
Figure 4. Fluorescence emission spectra of **SP-OPV-SP** (**10**), (A) in ACN solution (~60 µM) and (B) as a film onto quartz plate at room temperature excited at 415 nm. (a) black curve, before irradiation of UV light, (b) magenta curve, after irradiation of UV light (350 nm)for 10 min in ACN solution and for 10 second in film and (c) orange curve, after Visible light irradiation at 580 nm for 2 min in ACN solution and 570 nm for 10 min in film (d) blue curve, addition of 2 equivalent of CF_3COOH immediate after UV irradiation respectively. Inset 1 in (A) shows the enlarge view of tail end of emission spectra where emission from **MC** form of **SP** could be visible, Inset 2 in (A) and Inset 1 in (B) show the reversible modulation of fluorescence intensity of **OPV** moiety at 470 nm of dyad **SP-OPV-SP (10)** in ACN solution and in cast film respectively

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 µ M) 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 4S). A red shift of emission maxima of dyad **10** is observed with respect to the emission peak of reference **OPV (7)** (ESI, Figure 4S). 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 350 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_3COOH 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

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_3COOH 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**) resemblances the typical **OPV** fluorescence characteristic in film form[37] (see ESI Figure4S). 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 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_3COOH 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 fluoremeter and replaced back after having CF_3COOH 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 the 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 quenchs 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. Upon addition of 2 equiv of CF_3COOH (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 fluorescent 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 invent 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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