Electronic Supplementary Information

Peptide based two component white light emitting system

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Schemes and Synthesis procedures:

(1) Synthesis of Methyl 4-(4-aminostyryl) benzoate (6): Compound 6 has been

synthesized according to the **scheme 1** as following:



The experimental procedures are described elsewhere in the reference 12 of main paper.

Characterization datas:

Compound 3: ¹H NMR (500MHz, CDCl₃): δ 7.56 (d, J = 8.5 Hz, 2H), 7.14 (d, J = 8.5 Hz, 2H), 6.48 (s, 1H), 1.50 (s, 9H). Anal. Calcd. for C₁₁H₁₄INO₂ : C, 41.4; H, 4.42; N, 4.39. Found C, 41.46; H, 4.44; N, 4.36. HRMS calcd for C₁₁H₁₄INO₂ [M+Na]⁺ 341.996, found 341.946.

Compound 4: ¹H NMR (500MHz, CDCl₃) δ 7.99 (d, J = 8 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H), 6.74 (dd, J = 10.5 and 17.5 Hz, 1H), 5.85 (d, J = 17.5 Hz, 1H), 5.37 (d, J = 11 Hz, 1H), 3.90 (s, 3H). Anal. Calcd. for C₁₀H₁₀O₂ : C, 74.06; H, 6.21. Found C, 74; H, 6.18.

Compound 5: ¹H NMR (300MHz, CDCl₃) δ 8.01 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 16.2 Hz, 1H), 7.02 (d, J = 16.2 Hz, 1H), 6.58 (s, 1H), 3.92 (s, 3H), 1.53 (s, 9H). ¹³C NMR (75MHz, CDCl₃): δ 167.09 (COOMe), 152.69 (Boc C=O), 142.19, 138.56, 131.73, 130.82, 128.74, 127.67, 126.26, 118.69, 80.91, 52.18. FT-IR (cm⁻¹): 3370.8, 2973.5, 1715.8, 1600, 1586, 1523.4, 1436.3, 1416.5, 1366.8,

1315.12, 1281.8, 1233.5. Anal. Calcd. for $C_{21}H_{23}NO_4 : C, 71.37; H, 6.56; N, 3.96$. Found C, 71.31; H, 6.51; N, 3.88. HRMS calcd for $C_{21}H_{23}NO_4 [M+Na]^+$ 376.152, found 376.158.

Compound 6: ¹H NMR (500MHz, DMSO-d₆): δ 7.99 (d, J = 7.5 Hz, 2H), 7.51 (d, J = 8 Hz, 2H), 7.36 (d, J = 8 Hz, 2H), 7.13 (d, J = 16 Hz, 1H), 6.93 (d, J = 16.5 Hz, 1H), 6.69 (d, J = 8 Hz, 2H), 3.92 (s, 3H), 1.53 (s, 9H). ¹³C NMR (125MHz, DMSO-d₆): δ 167.16 (COOMe), 146.91 (ArC-NH₂), 142.76, 131.47, 130.13, 128.30, 127.54, 125.98, 124.01, 115.32, 52.12. Anal. Calcd. for C₁₆H₁₅NO₂ : C, 75.87; H, 5.97; N, 5.53. Found C, 75.81; H, 5.95; N, 5.58. HRMS calcd for C₁₆H₁₅NO₂ [M+Na]⁺ 276.099, found 276.105.

(2) Synthesis of Boc-Leu-Val-Phe-OMe (12): Compound 12 has been synthesized according to the scheme 2 as following:

(a) Synthesis of Boc-Leu-OH (7): L-leucine (13.1 g, 100 mmol) was added in a mixture of dioxane (100 mL), water (100 mL) and 1 N NaOH (200 mL) and then this was stirred for 5 min and cooled in an ice-water bath. $(Boc)_2O$ (24 g, 110 mmol) was added and stirring was continued at room temperature for 6 h. Then the solution was concentrated in vacuum to about 200 mL, cooled in an ice water bath, covered with a layer of ethyl acetate (about 400 mL) and acidified with a dilute solution of KHSO₄ to pH 2-3 (Congo). The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na₂SO₄ and evaporated in vacuum. A white gummy material was obtained (18.5 g, 80 %).

(b) Synthesis of H₂N-Val-OMe (8): In a round-bottom flask fitted with a CaCl₂ guard tube SOCl₂ (30 ml) was added to 300 ml of MeOH drop wise at ice cold condition and then the mixture was stirred for 5 min. After that L-valine (23 g, 200 mmol) was added to this solution. The reaction mixture was stirred for 6 h and solvent was distilled out to get a white solid. This solid was dissolved in water and cooled to 0 °C. Then the water layer was covered with a layer of ethyl acetate (about 500 ml) and basified with a dilute solution of Na₂CO₃. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na₂SO₄ and evaporated in vacuum to get the solid product (14.2 g, 55 %).

(c) Synthesis of Boc-Leu-Val-OMe (9): Boc-Leu-OH (18 g, 79 mmol) was dissolved in a mixture of 25 mL of dimethylformamide (DMF) in an ice water bath. H₂N-Val-OMe (14.2 g, 90

mmol) was dissolved in minimum volume of ethyl acetate and it was then added to the reaction mixture, followed by 16.5 g (80 mmol) of DCC immediately. The reaction mixture was allowed to come to room temperature and it was stirred for 48 h. Dicyclohexylurea (DCU) was filtered off from the reaction mixture. To the filtrate ethyl acetate (500 mL) was added and the organic layer was washed with 2M HCl (3×200 mL), 1N sodium carbonate (3×200 mL) and brine (2×200 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum. The crude product obtained was purified by silica gel column chromatography (5% EtOAc/CHCl₃) to afford pure Boc-Leu-Val-OMe (**9**) as a white solid (20.6 g, 75 %).

¹H NMR (400 MHz, CDCl₃): δ 6.62 (d, J = 8 Hz, NH, 1H), 4.93 (d, J = 7.6 Hz, NH, 1H), 4.53-4.49 (m, C_a H, 1H), 4.10 (br, C_a H, 1H), 3.71 (s, OMe, 3H), 2.18-2.12 (m, C_b H, 1H), 1.68-1.61 (m, C_b H, 2H), 1.48-1.47 (m, 1H), 1.42 (s, Boc-CH₃, 9H), 0.94-0.88 (m, -CH₃ Hs, 12H). HRMS calcd for C₁₇H₃₂N₂O₅ [M+Na]⁺ 367.220, found 366.796.

(d) Synthesis of Boc-Leu-Val-OH (10): To 20.6 g (60 mmol) of Boc-Leu-Val-OMe in 100 mL of MeOH and 60 mL of 1M NaOH were added, and the progress of saponification was monitored by thin layer chromatography (TLC) with time. The reaction mixture was stirred. After 10 h, methanol was removed under vacuum and the residue was taken in 100 mL of water and washed with diethyl ether (2×50 mL). Then the pH of the aqueous layer was adjusted to 2 using dropwise addition of 1M HCl, and it was then extracted with ethyl acetate (3×200 mL). The extract was pooled, dried over anhydrous sodium sulfate, and evaporated under vacuum to yield a white gummy compound (15 g, 80%).

¹H NMR (500 MHz, DMSO-d₆): δ 11.45 (br, -COOH, 1H), 7.66 (d, *J* = 8 Hz, NH, 1H), 6.88 (d, *J* = 8.5 Hz, NH, 1H), 4.11-4.03 (m, C_{\alpha} H, 2H), 2.02-1.98 (m, C_{\beta} H, 1H), 1.53 (br, C_{\beta} H, 1H), 1.38 (br, C_{\beta} H, 1H), 1.31 (s, Boc-CH₃, 9H), 0.81-0.78 (m, -CH₃ Hs, 12H).

¹³C NMR (125MHz, DMSO-d₆): δ 173.64 (COOH), 173.39 (CONH), 156. (Boc C=O), 79.12, 57.40, 53.39, 40.90, 30.62, 28.64, 24.71, 23.31, 21.91, 19.35.

HRMS calcd for $C_{16}H_{30}N_2O_5 [M+Na]^+$ 353.205, found 353.213.

(e) Synthesis of H₂N-Phe-OMe (11): In a round-bottomed flask fitted with a $CaCl_2$ guard tube $SOCl_2$ (15 ml) was dropwise added to 150 ml of MeOH in ice-cold condition and then the mixture was stirred for 5 min. After that L-phenylalanine (16.5 g, 100 mmol) was added to this

solution. The reaction mixture was stirred for 6 h and the solvent was distilled out to get a solid mass. This mass was dissolved in water and cooled to 0 $^{\circ}$ C. Then the water layer was covered with a layer of ethyl acetate (about 100 ml) and basified with a dilute solution of Na₂CO₃. The aqueous phase was extracted with ethyl acetate and this operation was done repeatedly for a few times. The ethyl acetate extracts were pooled, washed with water and dried over anhydrous Na₂SO₄ and evaporated in vacuum to get the solid product (8.95 g, 50 %).

(f) Synthesis of Boc-Leu-Val-Phe-OMe (12): Boc-Leu-Val-OH (15 g, 45 mmol) was dissolved in a mixture of 25 mL of dry DMF in an ice water bath. H₂N-Phe-OMe (8.95 g, 50 mmol) was dissolved in minimum volume of ethyl acetate and it was then added to the reaction mixture, followed by the addition of 9.27 g (45 mmol) of DCC immediately. The reaction mixture was allowed to come to room temperature and it was stirred for 48 h. Dicyclohexylurea (DCU) was filtered off, from the reaction mixture. To the filtrate ethyl acetate (100 mL) was added and the organic layer was washed with 2M HCl (3×50 mL), 1N sodium carbonate (3×50 mL) and brine (2×50 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum. The crude product obtained was purified by silica gel column chromatography (5% EtOAc/CHCl₃) to afford pure Boc-Leu-Val-Phe-OMe (**12**) as a white solid (15.47 g, 70 %).

¹H NMR (500MHz, CDCl₃): δ 7.27-7.09 (m, 5H), 6.99 (m, 2H), 6.75 (d, J = 8.5 Hz, NH, 1H), 6.69 (d, J = 8.5 Hz, NH, 1H), 5.07 (d, J = 8.5 Hz, NH, 1H), 4.86-4.82 (m, C_α H, 1H), 4.29-4.26 (m, C_α H, 1H), 4.10 (br, C_α H, 1H), 3.68 (s, -OCH₃, 3H), 3.09-3.04 (m, C_β H, 2H), 2.11-2.07 (m, C_β H, 1H), 1.68-1.57 (m, C_β H, 2H), 1.42 (s, Boc-CH₃, 9H), 0.93-0.85 (m, -CH₃ Hs, 12H). ¹³C NMR (125MHz, CDCl₃): δ 172.75 (COOMe), 171.79 (CONH), 170.76 (CONH), 155.88. (Boc C=O), 80.18, 58.43, 53.33, 52.36, 40.84, 38.05, 31.10, 28.42, 24.86, 23.09, 22.10. HRMS calcd for C₂₆H₄₁N₃O₆ [M+Na]⁺ 514.288, found 514.221.



(3) Synthesis of Boc-LVF-ST-OMe (1):



Synthesis of Boc-LVF-ST-OMe (1) has been done according to the scheme 3:

(a) Synthesis of Boc-Leu-Val-Phe-OH (13): To 5 g (10.2 mmol) of Boc-Leu-Val-Phe-OMe in 25 mL of MeOH and 10 mL of 1M NaOH were added, and the progress of saponification was monitored by thin layer chromatography (TLC). The reaction mixture was stirred. After 10 h, the reaction was complete and methanol was removed under vacuum. The residue was taken in 50 mL of water and washed with diethyl ether (2×50 mL). Then the pH of the aqueous layer was adjusted to 2 by using dropwise addition of 1M HCl, and it was then extracted with ethyl acetate (3×50 mL). The extract was pooled, dried over anhydrous sodium sulfate, and evaporated under vacuum to yield a white gummy compound (3.4 g, 70%).

(b) Synthesis of Boc-LVF-ST-OMe or Boc-Leu-Val-Phe-Stilbene-OMe (1): Boc-Leu-Val-Phe-OH (13) (0.12 g, 0.25 mmol) was dissolved in a mixture of 0.5 mL of N,Ndimethylformamide (DMF) in an ice water bath. Compound **6** (0.06 g, 0.24 mmol) was dissolved in minimum volume of ethyl acetate and it was then added to the reaction mixture, followed by the addition of 0.05 g (0.24 mmol) of DCC immediately. The reaction mixture was allowed to come to room temperature and it was stirred for 48h. Dicyclohexylurea (DCU) was filtered off and ethyl acetate was added to the filtrate. The organic layer was washed with 2M HCl (3×5 mL), brine (2×5 mL), and 1N sodium carbonate (3×5 mL) and brine (2×5 mL), dried over anhydrous sodium sulfate, and evaporated under vacuum to yield as a white solid. The crude product was purified by silica gel column chromatography (5% EtOAc/CHCl₃) to afford pure Boc-LVF-ST-OMe or Boc-Leu-Val-Phe-Stilbene-OMe (1) as a faint yellowish white solid (0.091 g, 51 %).

¹H NMR (500MHz, CDCl₃) δ 8.2 (d, J = 8 Hz, 2H), 7.96 (d, J = 8 Hz, 2H), 7.81 (d, J = 7.5 Hz, 2H), 7.36 (d, J = 7 Hz, 2H), 7.46-7.43 (m, 2H), 7.29-7.22 (m, 5H), 7.13 (d, J = 17 Hz, 1H), 7.12 (d, J = 17 Hz, 1H), 6.48 (br, NH, 1H), 4.85-4.84 (m, C_aH, 1H), 4.02-3.89 (m, C_aH, 2H), 3.48 (s, OCH₃, 3H), 3.16-3.09 (m, C_{β} H, 2H), 2.19-2.15 (m, C_{β} H, 1H), 2.04 (br, C_{β} H, 1H), 1.72 (br, C_{β} H, 1H), 1.43 (s, Boc-CH₃, 9H), 1.38-1.31 (m, 12H).

¹³C NMR (125MHz, CDCl₃): δ 175.85 (COOMe), 173.85 (CONH), 167.08 (CONH), 157.00 (Boc C=O), 141.08, 130.16, 129.58, 129.04, 128.74, 127.38, 126.60, 120.49, 81.29, 60.18, 52.18, 49.38, 34.06, 29.83, 28.45, 25.75, 25.07, 24.99, 23.07, 21.96.

HRMS calcd for $C_{41}H_{52}N_4O_7$ [M+Na]⁺ 735.373, found 735.376.

(4) Synthesis of MeO-FVL-PDI-LVF-OMe (2):

Synthesis of MeO-FVL-PDI-LVF-OMe (2) has been done according to the scheme 4:



(a) Synthesis of NH₂-Leu-Val-Phe-OMe (14): 2.46 g (5 mmol) of Boc-Leu-Val-Phe-OMe was dissolved in 10 ml trifluoro acetic acid (TFA) at 0°C. It was then stirred for overnight at room temperature. Then TFA was removed in vaccuum and the residue obtained, was dissolved in 50 ml ethyl acetate. The organic layer was extracted with sodium carbonate solution (2 X 50 ml) followed by brine solution (2 X 50 ml). The organic layer was dried over anhydrous sodium

sulfate and it was then evaporated under vaccuum to obtain the product as a white solid mass (1.56 g, 80 %).

(b) Synthesis of MeO-FVL-PDI-LVF-OMe (2): 1.56 g (4 mmol) NH₂-Leu-Val-Phe-OMe (14) and 392 mg (1 mmol) Perylene tetracarboxylic bisanhydride were mixed together very well, then 544 mg (8 mmol) imidazole was added to it. The reaction mixture was heated to 120°C under inert atmosphere and it was stirred for overnight. Then reaction mixture was cooled to room temperature and the residue was washed well with chloroform. The filtrates were collected and washed with (4 X 50 ml) 1N HCl solution followed by (2 X 50 ml) brine solution. The organic layer was dried over anhydrous sodium sulfate and evaporated under vaccuum to obtain the crude product as a brownish red solid. The crude product was purified by silica gel column chromatography (5% MeOH/CHCl₃) to afford pure MeO-FVL-PDI-LVF-OMe or MeO-Phe-Val-Leu-PDI-Leu-Val-Phe-Ome (2) as deep red solid (0.32 g, 28 %).

gummy compound (15 g, 80%).

¹H NMR (500 MHz, CDCl₃): δ 8.56 (br, PDI core Hs, 4H), 8.44 (br, PDI core Hs, 4H), 7.28-6.99 (m, 10H), 5.81 (br, NH, 2H), 5.06 (br, NH, 2H), 4.86-4.82 (m, C_aH, 2H), 4.29-4.26 (m, C_aH, 2H), 4.10 (br, C_aH, 2H), 3.68 (s, -OCH₃, 6H), 3.09-3.04 (m, C_{\beta} H, 4H), 2.11-2.07 (m, C_{\beta} H, 2H), 1.68-1.44 (m, C_{\beta}H, 4H), 0.93-0.86 (m, -CH₃, 24H).

¹³C NMR (125MHz, CDCl₃): δ 176.60 (COOMe), 173.15 (CONH), 158.00 (imide C=O), 141.18, 130.96, 130.46, 129.18, 129.04, 128.91, 127.38, 126.38, 126.30, 120.19, 60.11, 52.18, 49.38, 34.08, 29.83, 28.48, 25.75, 25.09, 24.97, 23.17, 21.81.

HRMS calcd for $C_{66}H_{70}N_6O_{12}$ [M+Na]⁺ 1161.494, found 1161.607.

Instrumentation UV-Vis spectroscopic analysis.

We used a Cary Varian 50 scan UV-Vis optical spectrometer equipped with 'Cary Win' UV software to elucidate the optical properties of the solutions.

NMR Experiments.

All 300 MHz ¹H NMR and 75 MHz ¹³C NMR studies were carried out on a Brüker DPX 300 MHz spectrometer at 300 K. 500 MHz ¹H NMR and 125 MHz ¹³C NMR studies were carried out on a Brüker DPX 500 MHz spectrometer at 300 K. 400 MHz ¹H NMR studies were carried out on a Brüker DPX 400 MHz spectrometer at 300 K.

Mass Spectrometry.

Mass spectra were recorded on a Q-tof Micro YA263 high-resolution mass spectrometer.

Fluorescence spectroscopy.

Fluorescence studies of the solution in a sealed cuvette were carried out in a Perkin Elmer LS55 Fluorescence Spectrometer instrument. All the experiments were carried out with the excitation slit width 2.5 nm and emission slit width 15 nm.

Actual quantum yields have been generally measured relative to an optically dilute standard fluorophore solution that exhibits a well-known quantum yield (ϕ_s). The quantum yield of an unknown fluorophore (ϕ_u) has been determined using the parker-rees method.

$\phi_u = (A_s F_u n_u^2 / A_u F_s n_s^2) \times \phi_s$

Where, A_u denotes the absorbance of the unknown sample at the excitation wavelength, F_u represents the total integrated fluorescence intensity for the unknown sample, when it is excited at the same excitation wavelength of the unknown sample, F_s is the integrated fluorescence intensity of the reference sample, when it is excited at the same excitation wavelength of the known sample. Refractive index of solvent in which the unknown and the standard samples have been prepared, are given by n_u and n_s respectively. To determine the quantum yield of the donor molecule **1**, stilbene was taken as the reference. Rhodamine B was taken as the reference for the determination of quantum yield of the acceptor molecule **2**.

Field Emission Scanning Electron Microscopy (FE-SEM).

Morphologies of the compounds 1, 2 and their equimolar mixture (1+2) were investigated by FE-SEM. For the SEM study, the solution was dried and coated with platinum. Then micrographs were taken in a SEM apparatus (JEOL microscope JSM-6700F).

Time-Correlated Single Photon Counting (TCSPC) study.

TCSPC measurements were performed by means of Horiba Jobin Yvon IBH having MCP PMT Hamamatsu R3809 detector instrument and all data were fitted using Data Station v2.3. We have used NANO-LED source for excitation of samples at 340 nm and LASER source for excitation of samples at 440 nm.



Figure S1: 500MHz ¹H NMR spectra of compound 1 in CDCl₃ at 298K.



Figure S2: 125MHz ¹³C NMR spectra of compound 1 in CDCl₃ at 298K.



Figure S3: HRMS mass spectra of compound 1.



Figure S4: 500MHz ¹H NMR spectra of compound 2 in CDCl₃ at 298K.



Figure S5: 125MHz ¹³C NMR spectra of compound 2 in CDCl₃ at 298K.



Figure S6: HRMS mass spectra of compound 2.



Figure S7: TCSPC plot of 1, 2 and white light emitting ODCB solution.

The energy transfer efficiency has been calculated from the TCSPC life time study using the following equation.¹³

$$E = 1 - \frac{\tau_{DA}}{\tau_{D}}$$

Where E is the energy transfer efficiency, τ_{DA} is the donor's lifetime (0.12 ns) in presence of the acceptor and τ_D is the donor's lifetime in absence of the acceptor (0.21 ns). The calculation shows that the energy transfer efficiency from donor **1** to the acceptor **2** is 43%.



Figure S8: (a) Overlap of emission spectra of **1** and absorption spectra of acceptor **2**. (b) Emission intensity change of donor **1** in presence of the same equivalent of acceptor **2** (both the solutions were excited at 343 nm).

In the figure 8b,

F_{DA}=1705.77553 and F_D=2946.93263

So, using the following equation we calculated the energy transfer efficiency value.

$$E = 1 - \frac{F_{DA}}{F_D}$$
E=0.42.

The calculation shows that the energy transfer efficiency from donor 1 to the acceptor 2 is 42%. From the above spectral overlap and energy transfer calculation, the Förster resonance energy transfer is convincingly proven from donor 1 to acceptor 2.



Figure S9: FE-SEM images of (a) 1, (b) 2 and (c) white light emitting solution.



Figure S10: Fluorescence emission of the acceptor (2) upon the gradual addition of donor at the excitation 343 nm showing significant spectral changes due to the energy transfer from donor to acceptor.

The absorption at 343 nm of the acceptor molecule is very low and investigation of the emission corresponding to this absorption peak has also been performed. The excitation and emission slit widths have been changed (ex. slit: 2.5, em. slit: 15) to examine the spectral changes associated for the low emission intensity of the acceptor 2 in solution. It is evident from the figure S10 that the addition of the donor molecule 1 to the acceptor 2 solutions causes increase in emission intensity of the acceptor due to FRET. So, in absence of the donor the acceptor molecule exhibits very low intensity emission at the excitation of 343 nm. However, due to FRET from donor 1 to acceptor 2 the intensity of emission increases.



Figure S11: Comparison between the UV absorption spectrum and PL excitation spectrum of the white light emitting solution. (Equivalents of donor: acceptor = 1.0:1.0 for both the cases)

To depict the FRET phenomenon from donor 1 to acceptor 2, a comparison between the UV-Vis absorption spectra and PL excitation spectra has been done for the white light emitting solution

by keeping 1:1 equivalent of donor: acceptor. It is evident from the figure S11 that the intensity of excitation for the acceptor molecule 2 is decreased due to the FRET phenomenon.



Figure S12: Fluorescence emission of the acceptor 2 in presence of varying concentrations of donor 1 showing the significant spectral changes due to the energy transfer from donor to acceptor. It also indicates the interaction between donor and acceptor.

To explain the increase in the average lifetime of the acceptor molecule 2, the interaction of the acceptor 2 in presence of the donor has been investigated. Gradual addition of the donor to acceptor molecule was done for this purpose. All emission spectra are recorded at the excitation of 537 nm (at the major excitation wavelength of acceptor 2). The figure S12 shows that gradual addition of donor 1 to acceptor 2 results in an increase in intensity of the emission of the acceptor 2. This is due to the interaction between donor and acceptor molecules. The increased lifetime of the acceptor molecule may be due to the equilibrium with the other excited states of the acceptor of similar energy and also due to the interaction with the donor molecule. ^{S1, S2}

S1. S. Bhattacharyya, B. Paramanik, .A. Patra, J. Phys. Chem. C 2011, 115, 20832.
S2. T. Mondal, A. K. Das, D. K. Sasmal, K. Bhattacharyya, J. Phys. Chem. B 2010, 114, 13136.