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White Light Emission in Water through Admixtures of Donor-π-Acceptor Siblings: Experiment and Simulation

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Abstract:

Donor-acceptor π -conjugated molecules with triphenylamine donor and different acceptor (H, Cyano, and Pyridinium) units with a double bond spacer were synthesized. These compounds exhibit bathochromic shifts in absorption and emission with an increase in the acceptor strength. Solvatochromic measurements in water reveal emitting states characterized by a polar nature with three distinct emission spectral regions from blue to red. Interestingly, binary mixtures of the stilbenes in acetonitrile and water gave white light emission. MD simulations of the admixtures reveal that the emission data directly correlates to the structural arrangements of the molecules driven by intermolecular and solvent interactions with micelle-like structural arrangements for one set and uniform homogenous mixing for the other two sets. Such tunable emitting strategy using simple structural siblings could offer great potential towards designing novel emitting systems.

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Introduction

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Conjugated organic molecules with a delocalized π -system of electrons represent attractive targets for application in advanced functional materials¹⁻³. The ease of synthesis, tunable structure, and photoresponsive behavior of the π -conjugated systems allowed their extensive use in materials science for organic and biological applications⁴⁻⁹. The delocalization of π electrons in such organic molecules with donor (D) acceptor (A) framework causes intramolecular charge transfer yielding substituent dependent solvatochromic emission behavior with emission in blue, green, and red regions. This substituent dependent emission can be an ideal strategy to obtain white light emission through careful admixtures of different chromophores encompassing the visible range. White light emission is usually obtained by the blending of materials exhibiting complementary emission. Previously white light emission was demonstrated through the use of single molecular system bearing luminescent units^{10, 11}, binary or ternary mixtures^{12, 13}, phosphorescent systems¹⁴, modulation of pH¹⁵, use of organic-inorganic hybrid materials¹⁶, a combination of vegetable extracts^{17, 18}, selfassembly¹⁹⁻²¹, through supramolecular interactions²² and, covalent organic frameworks²³. However, issues about color quality, costs, stability, toxicity meant that research to achieve organic white-light-emitting molecular systems is still dominant^{24, 25}. Such fluorescent or luminescent materials have also been extensively utilized for biological applications. In this study, our strategy was based on the utilization of intramolecular charge transfer behavior of simple D- π -A molecular siblings to achieve tunable emission. In particular, we have used triphenylamine (TPA) as an electron donating group due to its favorable electron donating properties and facile synthetic strategies towards the incorporation of other substituents. The triphenylamine based molecular systems were a dominant scaffold for many organic electronic applications²⁶⁻³⁰. Incorporation of suitable electron acceptor unit combined with π bridge results in differential emission contributed by the extent of intramolecular charge transfer exerted by the donor or the acceptor group. Our study reveals that both substituents and solvents influence the emission properties resulting in blue-red emission. When combined in specific proportions, we were able to achieve white light emission in acetonitrile and water. To rationalize the experimental observations, MD simulations were carried out to understand the effect of substituted acceptor arm on molecular interactions in aqueous admixtures. Simulations revealed that emission spectra of admixtures correlate to the structural arrangement of molecules in admixtures. Such a strategy based on simple stilbene

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 molecular scaffold introduces a prospective way for white light emission with intramole Circle Online charge transfer characteristics without the need for identifying blue or red emitting materials. The results are detailed below.



Scheme 1: The synthetic pathways towards the synthesis of formyltriphenylamine and stilbene derivatives (1-3).

Experimental

All the chemicals, reagents used in this study were purchased from Sigma Aldrich, Alfa Aesar, Acros, and S. D. Fine Chemicals. UV-Vis absorption spectra were recorded using Analytik Jena specord 210 plus, and the fluorescence emission studies were performed using Horiba-Jobin Yvon Fluolorog-3 spectrofluorometer with a slit-width of 1 nm. ¹H and ¹³C NMR spectra were obtained with a Bruker Avance 500 MHz NMR spectrometer. For the absorption or fluorescence studies, 10 μ L of the desired fluorophore-stock solution in dioxane (~10⁻³ M) was added to 1 mL (effective concentration ~10 μ M) of the desired solvent media. The excitation wavelengths were set at the absorption maxima (λ_a) of the compounds under investigation and the emission (λ_t) reported is uncorrected, and measurements were performed at room temperature. Scanning electron microscopy (SEM) analysis was carried out using a field emission SEM (JSM 7600F JEOL). For this purpose, one drop of the sample [~10 μ M solutions] was deposited on a Si-wafer mounted on an aluminum stub with the help of double-sided adhesive carbon tape. The samples were dried at room temperature for 12 h and coated with platinum before being analyzed. For powdered sample analysis, dried powered sample was sprinkled on the surface of carbon tape and coated with platinum

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before analysis.

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Computational Methodology: The 3D coordinates for all three molecules, were generated by using GaussView³¹ software followed by geometry optimization at HF/6-31G* level. The partial atomic charges and the parameters for potential energy function were derived from OPLS-AA force field³². All MD simulations were carried out by using Gromacs package³³. Water molecules were represented by the TIP3P water model, which describes water as three-point with rigid pair potentials³⁴. After performing energy minimization using steepest descent algorithm, each system undergoes NVT for 300ps followed by NPT equilibration run for 300 ps. With a step size of 1 fs $(10^{-15}s)$ throughout the simulations, the temperature was controlled at 300K using Langevin dynamics and pressure is maintained at 1 bar using isotropic pressure coupling with Parrinello-Rahman³⁵ barostat at each 2 ps. Long-range interactions were evaluated by particle mesh Ewald³⁶ in reciprocal space while short-range van der Waals interactions were truncated at 1 nm. To eliminate the wall effect, periodic boundary conditions were employed in XYZ directions, and all bond lengths were constrained via the LINCS algorithm³⁷. Single molecule dynamics were studied in a cubical box with 4334 water molecules whereas one counter ion was added to the charged molecular system to maintain electrical neutrality. For studying molecular interactions in water, we choose a total of 60 molecules in the 8x8x8 nm³ cubical box with around 50000 water molecules and a respective number of counter ions to neutralize the system. Similarly, all three binary mixtures were simulated with a 1:1 ratio of participating molecules with a total of 60 molecules. The emission spectra were calculated by using M062x DFT functionals³⁸ with 6-311++G(2d,2p) basis set whereas instead of representing a huge number of water molecules explicitly, polarizable continuum model calculations using the integral equation formalism approach³⁹ was employed in Gaussian.

Synthetic Methods

The synthetic strategy for the synthesis of the stilbenes is given in scheme-1.

Synthesis

4- (diphenylamino) benzaldehyde (4): POCl₃ (53 mmol, 5 mL) was added dropwise to 20 mL of dry DMF at 0°C with continuous stirring and after raising the temperature to 75°C, triphenylamine (40.7 mmol, 10 g) and stirred for 2.5 h. After allowing the contents to warm

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up to room temperature, the reaction mixture was neutralized by NaOH and extracted with the organic layer was dried using anhydrous sodium sulfate and concentrated under reduced pressure. The desired product is obtained after chromatography purification (silica gel with 1:10 v/v CH₂Cl₂: petroleum ether). Yield 8.60 g (70%). (White color powder, 0.838 gm, yield 67.2%). ¹HNMR (500 MHz, CDCl₃, δ ppm) δ 8.79-8.78 (d, *J* = 6.5 *Hz*, 2H), 8.165-8.152 (d, *J* = 6.5 *Hz*, 2H), 4.66-4.63 (t, *J* = 15 *Hz*, 2H) 3.51 – 3.48 (m, *J* = 15 *Hz*, 2H), 3.15 (s, 9H), 2.64 (s, 3H), 2.59-2.53 (m, 2H), 3.08 (s, 6H); ¹³C NMR (125 MHz, CDCl₃, δ ppm) 153.58, 150.09, 145.24, 142.05, 136.42, 130.68, 130.13, 128.84, 127.27, 125.97, 124.42, 123.41, 121.19, 117.01, 105.89, 47.8.

General procedure for Stilbenes 1 & 2: *para*-substituted benzyl bromide and triethyl phosphite $[P(OEt)_3]$ was dissolved in 20 ml of dry THF and stirred for 30 h at 75°C. The reaction mixture was cooled to room temperature, and the solvent was concentrated under reduced pressure. Sodium hydride (5 equiv) in ~20 ml of dry THF was added to the reaction contents at 0°C and stirred for 15 min. The temperature was raised to 75°C, and formyltriphenylamine was added, and the reaction was stirred for 30 h. The contents were then cooled and extracted using dichloromethane, dried using anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification using silica gel column chromatography (2.5:10 v/v with CH₂Cl₂: Petroleum ether) yielded the desired products.

N,N diphenyl 4-styrene (1): (whitish-green powder, 0.838g, yield 67%). ¹H NMR (500 MHz, DMSO-D6, δ ppm) 7.581-7.566 (2H, d, J=7.5 Hz), 7.531-7.514 (2H, d, J=8.5Hz) 7.384-7.353 (t, J = 7.5 Hz, 2H), 7.342-7.31 (t, J=8Hz, 4H), 7.262-7.23 (t, J = 7.5 Hz, 1H) 7.224-7.191 (d, J=16.5 Hz, 1H), 7.138-7.106 (d, J-16 Hz, 1H), 7.075-7.039 (m, J = 8 Hz, 6H); 6.977-6.96 (d, J=8.5 Hz, 2H)., ¹³C NMR (125 MHz, CDCl₃, δ ppm) 147.45, 147.22, 137.77, 131.82, 130.06, 129.16, 128.37, 128.10, 127.79, 127.34, 126.72, 124.60, 123.74, 123.50. Calcd for C₂₆H₂₁N, 347.1674; Found, 347.1706.

N,N diphenyl 4-cyano-styryl benzene (2): (yellow color powder, 0.87 g, yield 65%). ¹HNMR (500 MHz, CDCl₃, δ ppm): 7.611-7.596 (d, J = 7.5 Hz, 2H), 7.546-7.531 (d, J = 7.5 Hz, 2H), 7.392-7.377 (d, J = 7.5 Hz, 2H) 7.288-7.260 (m, J = 6.5 Hz, 4H), 7.166-7.122 (m, 5H), 7.073-7.042 (t, J = 7.5 Hz, 4H), 6.967-6.935 (d, J = 16 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃, δ ppm) 148.38, 147.30, 142.27, 132.48, 131.94, 130.00, 129.40, 127.86, 126.59, New Journal of Chemistry Accepted Manuscript

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124.90, 124.72, 123.50, 122.89, 119.18, 110.16. m/z (EI MS): Calcd for $C_{27}H_{20}N_{207,101059/29}$ Found, 373.1733.

4-(4-(diphenylamino)styryl)-1-methylpyridin-1-ium (3): The pyridinium derivative (3) was obtained by the condensation of 1-methyl-4-pyridinium iodide (2.9 mmol, 0.7 g) with (2) (2.9 mmol, 0.59 g) in ethanol (20 mL) containing piperidine and Zinc acetate (0.1mmol, 0.03 g). The reaction mixture was refluxed for 8h at 80°C and reaction was monitored with TLC till the complete consumption of starting material. Cooling of the reaction to room temperature yielded a red precipitate that is purified using column chromatography (dark red color powder, 0.42 g, yield 67%). ¹HNMR (500 MHz, CDCl₃, δ ppm) δ 8.864-8.851 (d, *J* = 6.5 Hz, 2H), 7.894-7.881 (d, *J* = 6.5 Hz, 2H), 7.637-7.605 (d, *J* = 16 Hz, 1H) 7.474-7.456 (d, *J* = 9 Hz, 2H), 7.344-7.313 (t, *J* = 8 Hz, 4H), 7.165-7.135 (m, *J* = 7.5 Hz 6H), 7.022-7.004 (t, *J* = 9 Hz, 2H), 6.959-6.927 (d, 1H, J-16 Hz), 4.486 (s, 3H); ¹³C NMR (125 MHz, DMSO, δ ppm) 153.90, 150.80, 146.41, 144.41, 142.14, 129.99, 129.64, 127.03, 125.86, 124.68, 123.29, 120.86, 118.90, 48.14. m/z (EI MS): Calcd for C₂₆H₂₃N₂, 363.1856; Found, 363.1866. The ¹H and ¹³ C NMR spectra are provided in the supporting information (Fig S7-S9)

Results and discussion

Absorption and emission properties

The absorption spectra of stilbenes 1-3 (Scheme-1) are given in Fig 1, and Fig S1 and Table 1 summarizes the absorption and emission data of the synthesized stilbenes. All the stilbenes are characterized by an electron donating triphenylamine moiety, connected to an aromatic ring by a π -bridge. Stilbene 1 has a phenyl group, stilbene 2 an electron withdrawing cyano group, and stilbene 3 has an electron withdrawing pyridinium group. In dioxane, stilbene 1 has maximum absorption (λ_{ab}) at ~368 nm, 2 absorb slightly longer (~390 nm), and 3 absorbs longest at 459 nm [Fig 1A]. All the stilbenes are characterized by a shorter wavelength band at 300 nm that is attributed to electronic transitions of the triphenylamine moiety alone⁴⁰. The order of the absorption maxima (3 >2> 1) directly correlates to the strength of the electron withdrawing group and reflects intramolecular charge transfer from donor to acceptor⁴⁰. Solvent polarity changes exert weaker (~2 to 7 nm) effects on the absorption maxima for the stilbenes. For 1 and 2, a broad absorption band is noted in water and this may be due to the aggregate formation⁴¹.

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Fig 1: a) Overlapped absorption spectra of stilbenes (1-3) in dioxane and b) absorption of stilbene 2 in various solvents. Absorption spectra of 1 and 3 in different solvents are given in the SI.

Solvent	1			2			3		
	λ_{abs}	$\lambda_f(nm)$	*¢ _f	λ_{abs}	$\lambda_{\rm f}(\rm nm)$	*¢ _f	λ_{abs}	$\lambda_{\rm f}(\rm nm)$	*¢ _f
	(nm)			(nm)			(nm)		
Heptane	366	399, 415	0.044	392	427, 454	0.351	462	-	
THF	367	437	0.058	390	494	0.271	459	626	0.131
Dioxane	367	425	0.069	390	462	0.341	461	592	0.364
CH ₃ CN	364	457	0.056	387	528	0.194	459	665	0.009
DMF	368	457	0.056	393	528	0.239	458	652	0.031
Methanol	364	452	0.055	391	520	0.179	468	639	0.017
Water	377	442	0.020	400	505	0.020	452	615	0.007
Solid	-	466		-	540			625	-

Table-1. Absorption and emission data of 1-3 in homogeneous solvents and solid state

*Fluorescence Quantum Yields were calculated using Quinine Sulfate (0.546 in 1N H₂SO₄) as a relative standard (for 1 & 2) and Rhodamine 6G, QY = 0.94 in EtOH for 3.

Emission in Solvents

In contrast to the weak absorption maxima changes, the stilbenes show strong solvatochromic emission due to intramolecular charge transfer (ICT) from a donor, triphenylamine group, to the acceptor (phenyl, cyano or pyridinium groups). The trends observed in the emission are also consistent with the strength of the electron withdrawing ability. Structured emission is noted for stilbenes **1** (399 and 415 nm) and **2** (427 and 454 nm) in heptane. Upon increasing the solvent polarity variable shifts in the emission, maxima were observed with smaller bathochromic shifts (~22 nm comparing dioxane to acetonitrile) for **1** and higher shifts (~54 nm) for **2** (Fig 2A & 2B). Stilbene **3** with pyridinium group (Fig 2C) shows strongest bathochromic emission shifts (~73 nm) with emission maxima > 600 nm in polar solvents.

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The solvent polarity bathochromic shifts are attributed to the strong ICT character of the strong ICT character of the strong is stabilization through solvent-solute interactions⁴².



Fig 2. Emission spectra of stilbenes 1(A), 2 (B) and 3 (C) in solvents of different polarity

Emission in binary solvent mixtures and Scanning Electron Microscopy studies

To understand the effect of solvent polarity changes and to learn of the aggregation behavior, we measured the emission of the stilbenes in dioxane (non-polar) & water (polar) binary solvent mixture. With an increase in solvent polarity by addition of water in dioxane, gradual emission shifts were observed (Fig S2). For 1, the emission maxima shifts from 427 nm in dioxane to 459 nm (70% water) and 445 nm at 100% water with overall emission shifts of 20 nm. Moreover, a significant drop (~40 fold) in intensity is noted indicating emission quenching. Stilbene 2 also shows a similar behavior: 469 nm in dioxane to 540 nm at 70% water that is lowered to 505 nm in 100% water with a ~27 fold decrease in emission intensity. These emission losses are due to aggregation induced quenching⁴³ unlike their structural siblings, α -cyanostilbenes, where the opposite aggregation induced emission, is

observed^{13, 44, 45}. Stilbene **3** with cationic pyridinium group showed greater emission of the second component.



Fig 3. Scanning Electron Microscopy (SEM) images of stilbenes 1-3 (10µM) in water.

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Emission of molecular mixtures in acetonitrile and water: White Light Emission

The emission data (Table-1) reveals that Stilbene 1 with no electron withdrawing substituents emits in the violet, 2 with nitrile substituent emits in the cyan and 3 in the red region. We implied that the mixing of these fluorophores should enable tunable emission behavior. To test this, we performed a titration of the molecules with one another in water and recorded their emission spectrum. Titration of 1 with 2 shows gradual emission shifts with increased addition of the second fluorophore. Stilbene 1 emits at ~445 nm in water and stilbene 2 emits at ~505 nm. Gradual addition of 2 yields emission shifts with emission bands were not observed corresponding to the two molecules for the mixtures [Fig 4]. The emission titration with 2 and 3 reveal similar features. Stilbene 2 emits at ~505 nm in the water while stilbene 3 emits at 614 nm. Gradual emission shifts with distinct emission maxima different to either molecule culminating at 530 nm are observed.



Fig 4: Binary mixture titrations of the molecules in water A (1 and 2), B (2 and 3) and C (1 and 3). Individual emission spectra obtained for 1, 2 and 3 are given as dotted lines.

Titration of stilbene **1** with **3** shows slightly different behavior. Increased addition of **3** with different behavior. Increased addition of **3** with a shorter wavelength of the shows a slight hypothese of a second emission band at a longer wavelength. The 445 nm shows a slight hypothese shift to ~435 nm while the longer wavelength band shows emission maxima at ~530 nm which is still adrift by 80 nm from the individual emission maxima of **3**. The intermolecular interactions of the fluorophores coupled with solvent interactions result in the observed unique emission. The binary mixture titration experiments were also repeated in acetonitrile where all the stilbenes are readily soluble (Fig S3). Titration of **1** with **2** shows the initial emission at 459 nm that shifts to ~519 nm upon addition of **2** with the appearance of shoulder band at 460 nm. Titration of **1** with **3** yield emission maxima at 553 nm (**3** alone emits at 665 nm) culminating with distinct bands at 1:2 proportions of **1** and **3** with a shorter wavelength band at ~452 nm and the titration of **2** and **3** yield distinct emission maxima at 567 nm.



Figure 5 (A). CIE plots of binary mixtures **1** & **3** obtained through the mixing of two different components 1 and 3 in water. **5B**. CIE plot for stilbenes 1-2 mixtures in acetonitrile at different concentrations (data points 1 to 6 are for different concentrations). The coordinates and the concentrations used are given in the supporting information [Table-S2]. The white light emission shown is visualized under UV light (using 312 nm light on a transilluminator).

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mixtures was generated using RGB (Red, Green, and Blue) color space diagram⁴⁷_{DCI}. The Vertice Online values indicate that observance of good white light emission coordinates for the combination of the stilbenes (1 and 3) at different concentrations [Fig 5A] while for stilbenes 1 and 2 in acetonitrile show coordinates close to white light emission [Fig 5b]. This approach of using simple structural siblings could be of great utility for generating tunable emissions and white light emission

Emission in Solid State

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Stilbenes with Donor-acceptor substituents with good absorption and emission behavior have been extensively investigated as organic materials^{3, 48}. We, therefore, measured the emission of monomers and mixtures in the solid state to check if they yield tunable and or white light emission. In solid state, 1 emits at 466 nm corresponding to the blue region, 2 at 541 nm in the green region and 3 emits at 623 nm corresponding to the red region. These emission maxima are red-shifted concerning the emission maxima in water. Better packing interactions and increase in effective conjugation length due to greater planarity in the solid state result in the red-shifted emission as compared to the solution state. For mixtures, 10 mg of each molecule was ground and dissolved in dioxane. After drying the annealed mixture, the emission measurements were performed. The emission spectra given in Fig 6b shows an emission maximum at 564 nm and a band at 505 nm for mixtures of 1-2; 627 nm and a weak band at 509 nm for 2 & 3; and 644 nm for 1-3. These emission bands show distinct deviations from the original solid state emission wavelengths. Lastly, the mixture of 1+2+3 yields emission bands at 599 nm and 507 nm. Thus by mixing of the different substrates, tunable emission is obtained, but solid-state white light emission was not obtained unlike in water or acetonitrile in solution. In substrates where intramolecular charge transfer is involved, it is likely that solvent effects play a cooperative role along with the binary components yielding tunable emission.

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Fig 6. Emission in the solid state (A) of individual molecules and the mixtures (B). The excitation wavelength used is the absorption maxima of individual fluorophores

Rationalization of observations through MD Simulations: Emission in water

Charge difference across the acceptor arm of all three molecules governs the emission behavior of molecules. To analyze the distribution of water molecules around each molecule, we calculated pair distribution function g(r) using trajectories of single molecule MD simulation. Radial distribution function $g_{ij}(r)$ gives the relative probability (compared to that of an ideal gas) of finding molecule j around a molecule i within a spherical shell of thickness δr at a radial distance r. In the following study, i represent the molecules **1**, **2** and **3** and j represents water molecules. $g_{ij}(r)$ from now on is represented as g(r).

Computed g(r) shows significant (Fig 7) difference in water population at the first hydration shell among three molecules. Compared to 1 and 2, positively charged nitrogen atom in acceptor's arm in 3 is responsible for attracting water molecules from the intermediate shell to first hydration shell evident by the higher peak in Fig 7. Intermolecular interaction with water molecule can affect the conjugation between donor and acceptor arm of the molecule by altering the angular geometrical between donor and acceptor arm. To understand the binary mixture interactions, we analyzed the distribution of geometrical angles between donor and acceptor arm. Superimposition of atomic coordinates (Fig S5) shows significant differences in the geometry of acceptor arms of all three molecules.

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Figure 7: Radial distribution function g(r) between the stilbenes 1,2 and 3 with water. Stilbene 3 has a stronger interaction with water due to the presence of charged N group which is evident from the peak at 0.5nm.

We computed the dihedral angles (Fig S6) for describing the ring-twists and found that the aromatic rings on the donor's arm have similar geometries, but the presence of the water molecule significantly affects the planarity of the acceptor's arm. Interaction of positively charged N atom in acceptor arm of **3** leads to a restriction in the rotational motion of the ring eventually favoring conjugation between the acceptor and π - linker. We also computed the absorption and emission wavelength using TDDFT calculations, and the resulting values are in good agreement with our experimental data (Table S1). Extended conjugation and strong interaction with the solvent minimizes the gap between the ground and excited state in molecule **3**. Moreover, theoretically computed energy differences among HOMOs and LUMOs (Fig S7) is decreasing from **1** to **3**, which is in line with the electron withdrawing nature of the acceptor's arm. To understand the structural arrangement of molecules in these aqueous admixtures, we calculated the radial probability distribution of the molecules in water.

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Fig 8: Radial distribution of molecular admixtures A(1-2), B(2-3) and C(1-3) in their aggregated state from the center of the aggregate which is obtained from 100 ns equilibrated MD run.

Equimolar mixtures of 1, 2 and 2, 3 show "like dissolves like" type mixing behavior as we move from the core to the exterior. The entire admixture in water maintains near spherical geometry throughout the production run. The probability distribution between 1 and 2 (Fig 8A) and (2 & 3: Fig 8B) matches quantitatively. However, we found that in a binary mixture of 1 and 3 (Fig 8C), both the molecules have their preferred structural arrangements, with the positively charged 3 tending to remain at the surface and the neutral 1 forming a hydrophobic core of the aggregate. This type of segregation in mixing gives rise to two independent bands as observed in experiments (Fig 4). To our knowledge, this is the first time MD simulations were used to understand the binary mixture containing Donor- π -acceptor siblings. Together

with our *in-silico* analysis reveals the role of acceptor's arm in the rearrangementiew Arcle Online molecules in binary mixtures that finally govern the emission of the mixtures.

Conclusions

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In summary, we demonstrate that by tuning donor or acceptor substituents on a simple stilbene scaffold, emissions ranging from blue to red are obtained through intramolecular charge transfer (ICT). Utilizing this ICT behavior, we observed white-light emission by careful mixing of the chromophores in water and acetonitrile. MD simulations in water reveal that the structural arrangements upon mixing the chromophores have a direct correlation on the emission spectra. Chromophores which interact favorably with each other (1&2 and 2 & 3) exhibit a single peak in the emission spectra governed by simple mixing rule. For admixtures, with one of the chromophores having preferential interaction with the solvent as in the case of Compound 1 &3 (*Water has a higher affinity towards 3 relative to 1*), we observe two unique peaks in the emission spectra that correlates directly to the formation of a micelle-type structure wherein we observe a core and shell populated by 1 and 3 respectively. This strategy of combining experiment and simulation to obtain tunable emission can be useful in designing newer materials for potential optical applications.

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Electronic Supporting Information: Fig S1-S9 and Tables S1 and S2 are provided.

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Graphical Abstract



White light emission through binary admixtures of push-pull stilbenes