# **Supporting Information**

# **Charge-Transfer Mediated J-aggregation in Red Emitting Ultra-Small-Single-Benzenic Meta-Fluorophore Crystal**

Mrinal Mandal,<sup>a,</sup> Sukumar Mardanya,<sup>a,</sup> Arijit Saha,<sup>a</sup> Manjeev Singh,<sup>a</sup> Swarnali Ghosh,<sup>a</sup> Tanmay Chatterjee,<sup>a</sup> Ramen Patra,<sup>a</sup> Surojit Bhunia,<sup>a,b</sup> Saptarshi Mandal,<sup>a</sup> Soumen Mukherjee,<sup>a</sup> Rahul Debnath,<sup>a</sup> C. Malla Reddy,<sup>a,b</sup> Mousumi Das,<sup>a,b</sup> and Prasun K. Mandal<sup>\*,a,b</sup>

<sup>a</sup>Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, West Bengal, India-741246. <sup>b</sup>Centre for Advanced Functional Materials (CAFM), Indian Institute of Science Education and Research (IISER) Kolkata, Mohanpur, West Bengal, India-741246. <sup>#</sup>These authors contributed equally. e-mail: prasunchem@iiserkol.ac.in

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#### **I. Experimental Procedures**

#### a. Chemicals used.

3-Nitrobenzaldehyde, Stannous chloride monohydrate and Malononitrile were procured from Sigma Aldrich. Ammonium formate was procured from TCI Chemicals. Methyl iodide and Ethyl iodide were procured from Spectrochem.  $K_2CO_3$ , KOH, DMSO, conc. HCl and KOH were procured from MERCK. Solvents used for spectroscopic measurements were of spectroscopic grade and were procured from Sigma Aldrich. Thin layer chromatographic (TLC) separations were performed on Merck Kieselgel 60 F254 plate using 100-200 mesh size silica gel.

#### b. Instrumentations.

**NMR details:** <sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub>, in Bruker AVANCE III 500 (500MHz) spectrometer. Chemical shift (δ in ppm) values are reported relative to tetramethylsilane (TMS) as internal standard (for <sup>1</sup>H NMR) to residual signal of the solvents (for <sup>1</sup>H NMR: CDCl<sub>3</sub>, 7.26 ppm; and for <sup>13</sup>C NMR: CDCl<sub>3</sub>, 77.0 ppm).

FTIR and MS details: IR spectra were recorded on a Bruker (model – ALPHA) FT-IR spectrometer. The HRMS data were obtained using a Bruker maXis II<sup>TM</sup> instrument.

**Crystallography:** Suitable single crystals of MF1 and MF2 were selected under microscope and mounted under nitrogen atmosphere using the X-TEMP2 and intensity data were collected on a Super Nova, Dual, Cu at zero, Eos diffractometer. The crystals of MF1 and MF2 were kept at 301K and 293 K respectively during data collection. Using Olex2,<sup>1</sup> the structure was solved with the ShelX<sup>2</sup> structure solution program using Intrinsic Phasing and refined with the ShelXL<sup>2</sup> refinement package using Least Squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic data (including structure factors) for the structures have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif. CCDC 2042111 and 2017383 contain the supplementary crystallographic data for MF1 and MF2 respectively.

**Powder X-ray diffraction (PXRD):** The PXRD data were collected on a Rigaku Smart Lab with a Cu K $\alpha$  radiation (1.54 Å). The tube voltage and amperage were set at 20 kV and 35 mA, respectively. Samples were scanned between 5 and 40° with step size of 0.5°. The instrument was previously calibrated using a silicon standard.

**Steady state optical spectroscopic measurements:** Steady state absorption spectra have been recorded in CARY Bio 300 UV-Visible Spectrophotometer. Corrected photoluminescence (PL) spectra have been recorded with Fluoromax-4, Horiba Jobin Yvon spectrofluorimeter and FLS 1000 fluorescence spectrometer (Edinburg Instruments). Solid state PL and absolute PL quantum yield measurements have been performed in FLS 1000 fluorescence spectrometer (Edinburg Instruments).

**Computational calculation details:** Computational calculations were performed using Gaussian 16 program.<sup>3</sup> The geometries of the ground-state for MFs 1-2 were optimized by the density functional theory (DFT) with the B3LYP hybrid function using 6-311 G (d, p) level of basis set. The ground state optimized geometries were used for vertical electronic absorption energy calculation using time-dependent density functional theory (TDDFT) with B3LYP hybrid function and same basis set.

#### c. Experimental details.

Solvatochromism and excited state dipole moment calculation: As *MFs* 1-2 exhibiting remarkable solvatochromism, Lippert-Mataga equation (*eq.* 1)<sup>4</sup> has been used to calculate excited state dipole moment. Lippert-Mataga equation is expressed as follows (*eq.* 1), where  $\bar{v}_{abs} - \bar{v}_{ems} = \Delta \bar{v}$  denotes the magnitude of Stokes shift,  $\bar{v}_{abs}$  and  $\bar{v}_{ems}$  correspond to the absorption and the emission maxima in terms of wavenumber (cm<sup>-1</sup>) respectively,  $\Delta \mu (= \mu_e - \mu_g)$  is the change of dipole moment between ground and the excited state, *h* is Planck's constant, *c* is the speed of light,  $\varepsilon$  and *n* are the dielectric constant and refractive index of the solvent respectively, and  $a_0$  is the Onsager cavity radius. Ground state dipole moment ( $\mu_g$ ) and the Onsager cavity radius ( $a_0$ ) have been obtained using DFT (B3LYP/6-311 g(d,p)) method.

$$\bar{v}_{abs} - \bar{v}_{ems} = \frac{2}{hca_0^3} \left( \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \right) \left( \mu_e - \mu_g \right)^2 \dots \dots \dots eq. 1$$

**Photoluminescence quantum yield calculation:** PLQY ( $\Phi$ ) of the *MFs* 1-2 in solution phase were calculated using relative quantum yield method using the following *eq.* 2, where  $\Phi$ , *OD*, *I* and *n* stand for quantum yield, optical density, integrated PL intensity, and refractive index of the solvent respectively. The subscript R refers to the reference. OD at each excitation wavelength has been kept at a value of 0.05 or lower. The standard used in these experiments are Coumarin 153 (reported PLQY = 58% in ethanol and  $\lambda_{ex}$  = 425 nm).<sup>4</sup> For QY calculation of each sample both the reference and the sample, same excitation wavelength have been used.

$$\Phi = \Phi_R \frac{I}{I_R} \frac{OD_R}{OD} \frac{n^2}{n_R^2} \dots \dots eq.2$$

**Time resolved optical spectroscopic measurements:** PL decay measurements were performed in time correlated single photon counting (TCSPC) module (Horiba Jibon Yvon IBH) using pico-second pulsed lasers ( $\lambda_{ex} = 405$  nm, FWHM <200ps) as the excitation sources and suitable TAC range values were chosen. An MCP photomultiplier tube (PMT) (Hamanatsu R3809U-50 series) was used as the detector. A nonlinear least-squares iterative reconvolution procedure using IBH-DAS6 software (version 2.2) was employed to fit the decay curves using a suitable exponential decay equation. The amplitude averaged PL decay lifetime ( $\tau_{avg}$ ) was calculated for every PL decay using the following *eq.* 3:

$$< au > = rac{\sum_i B_i \tau_i^2}{\sum_i B_i \tau_i} \dots \dots \dots \dots eq.3$$

where  $\tau_i$  is the excited state lifetime component and  $B_i$  is corresponding amplitudes of decay components.

**Nanoindentation:** Nanoindentation experiments have been performed on the single crystals using the TI Premier from Hysitron, Minneapolis, USA, equipped with an in-situ Scanning Probe Microscope (SPM). A Berkovich tip (three-sided pyramidal tip with a total included plane-edge angle of  $142.3^{\circ}$ ) of radius ~150 nm was employed to determine Young's modulus (*E*) and the hardness (*H*) of the crystals. The values of *E* and *H* were extracted using the standard Oliver-Pharr method.<sup>5</sup>

#### d. Synthesis and characterization.

The molecules have been synthesized following modified literature procedure.6



Scheme S1. Synthesis scheme of MFs 1-2.

#### Synthesis of 3-dialkylaminobenzaldehyde: 3-dialkylaminobenzaldehyde has been synthesized following reported procedure.<sup>7</sup>

To a solution of 3-Nitrobenzaldehyde (3.02 g, 20 mmol) in concentrated HCl (20 mL), SnCl<sub>2</sub> (7.5 g, 40 mmol) was added. Then, the reaction mixture was refluxed for 4 hour at 100°C. As the temperature increases, an orange coloured solution was obtained. The reaction mixture was filtered under vacuum in cold condition and washed with diethylether. The crude product was dried in desiccator overnight. This crude mixture was used for further alkylation reaction to get the final product without further purification.

The crude product dissolved in DMSO (15 mL) was added to the reaction mixture containing  $K_2CO_3$  (5.5 g, 40 mmol), KOH (1 g) and alkyl iodide (40 mmol) dissolved in DMSO (20 mL). The reaction mixture was refluxed for 8 hour at 80°C. After cooling, the resulting mixture was poured into cold water and extracted with DCM. The organic layer was concentrated under reduced pressure. Finally, the residue was purified by column chromatography on silica gel (hexane/EtOAc 20:1).

**Synthesis of 2-(3-(dimethylamino)benzylidene)malononitrile** (*MF*1): 3-dimethylaminobenzaldehyde (0.45 g, 3 mmol), malononitrile (0.21 g, 3.1 mmol) and ammonium formate (0.02 g, 0.31 mmol) were mixed in a hard glass microwave-resistant vessel. The mixture was subjected to microwave irradiation (Model MS2021CW, LG) for 90 seconds (with an installment of 30 seconds each at a power level of 300 Watts followed by intermittent cooling for 30 seconds). After completing the reaction (monitored by TLC on silica gel during cooling after each installment), crushed ice was added to the reaction mixture and stirred well. The crude product was then extracted with DCM and the organic layer was concentrated under reduced pressure. Finally, the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1). The yield of this reaction is 75%.

## *MF*1:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.72 (s, 1H), 7.35 (t, J= 8 Hz, 1H), 7.34, 7.27 (s, 1H), 7.11 (d, J= 8.2 Hz, 1H) 6.95 (dd, J= 8.5 Hz, 2.8 Hz, 1H), 3.02 (s, 6H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.27, 150.72, 131.62, 130.05, 119.48, 118.46, 114.06, 112.95, 112.24, 40.23. MS calculated for (C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>+H<sup>+</sup>): 198.1026, Found: 198.1029.

FT-IR (net) (cm<sup>-1</sup>): 2927, 2187, 1559, 1460, 1429.

**Synthesis of 2-(3-(diethylamino)benzylidene)malononitrile** (*MF2*): 3-diethylaminobenzaldehyde (0.53 g, 3 mmol), malononitrile (0.21 g, 3.1 mmol) and ammonium formate (0.02 g, 0.31 mmol) were mixed in a hard glass microwave-resistant vessel. The mixture was subjected to microwave irradiation (Model MS2021CW, LG) for 120 seconds (with an installment of 60 seconds each at a power level of 300 Watts followed by intermittent cooling for 30 seconds). After completion of reaction (monitored by TLC on silica gel during cooling after each installment), crushed ice was added to the reaction mixture and stirred well. The crude product was then extracted with DCM and the organic layer was concentrated under reduced pressure. Finally the residue was purified by column chromatography on silica gel (hexane/EtOAc 10:1). The yield of this reaction is 70%.

# *MF*2:

<sup>1</sup>**H** NMR (500 MHz, CDCl<sub>3</sub>): δ 7.70 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.26 (s, 2H), 6.99 (d, *J* = 7.3 Hz, 1H), 6.90 (dd, *J* = 8.5, 2.3 Hz, 1H), 3.39 (q, *J* = 7.1 Hz, 4H), 1.19 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 161.37, 148.25, 131.90, 130.24, 118.84, 117.98, 114.14, 112.96, 111.31, 44.51, 12.36. MS calculated for (C<sub>14</sub>H<sub>15</sub>N<sub>3</sub>+H<sup>+</sup>): 226.1339, Found: 226.1340.

**FT-IR (net) (cm<sup>-1</sup>):** 2927, 2187, 1559, 1460, 1429.

e. NMR data.



Figure S1. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of *MF*1 (see text for details).



Figure S2. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of MF2 (see text for details).









## **II. Results and Discussion**

# a. Literature reports of photophysical properties of popular dyes and red emitting single benzene based fluorophores.

Table S1. Photophysical properties of reported red emitting fluorophore (with two pairs of ortho-oriented CTD and CTA groups) having MW <400 Da (in solution phase).

Molecules	MW (Da)	Medium	$\lambda_{abs}^{max}$ (nm)	$\lambda_{em}^{max}$ (nm)	Stokes shift (nm)	Reference
R = NHMe	252	CHCl <sub>3</sub>	484	596	112	Angew. Chem. Int. Ed., 2017, <b>56</b> , 12543-12547
R = NHEt	280	CHCl <sub>3</sub>	485	599	114	Angew. Chem. Int. Ed., 2017, <b>56</b> , 12543-12547
NC CN	290	Acetone	457	562	105	Chem. Sci., 2017, <b>8</b> , 577-582
$ \begin{array}{ c c c } \hline & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & $	306	CH <sub>2</sub> Cl <sub>2</sub>	429	582	153	Chem. Commun., 2019, <b>55</b> , 11462- 11465
R = NHiPr	308	CHCl <sub>3</sub>	490	606	116	Angew. Chem. Int. Ed., 2017, <b>56</b> , 12543-12547
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	314	CH <sub>2</sub> Cl <sub>2</sub>	505	654	149	<i>Chem. Commun.</i> , 2019, <b>55</b> , 11462- 11465

 Table S2. Photophysical properties of popular red emitting dyes.4.8.9

Name of dyes	MW (Da)	$\lambda_{abs}^{max}$ (nm)	λ <sub>em</sub> <sup>max</sup> (nm)	Stokes shift (nm)	τ (ns)
Nile red	318	580	650	70	2.9
BODIPY 630/650	448	630	650	20	3.9
$\begin{array}{c} & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & &$	479	562	583	21	1.7
Mito-tracker red	496	579	599	20	1.8
ATTO 565	527	565	592	27	3.4
$\begin{array}{c} & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & &$	591	594	624	30	3.7
SO <sub>2</sub> NHX Texas Red	604	596	620	24	4.2
HO <sub>3</sub> S HO <sub>3</sub> S COX Alexa Fluor 594	706	590	617	27	3.9
$\overbrace{(CH_2)_3SO_3}^{O} (CH_2)_3SO_3 (CH_2)_3SO_3$	752	650	670	20	1.0

Generally, as per literature reports, red emission ( $\lambda_{em}^{max} \ge 600 \text{ nm}$ ) in solution phase has been observed with popular fluorophores having MW  $\ge 318$  Da. However, in this work we report red emission ( $\lambda_{em}^{max} \ge 600 \text{ nm}$ ) in solution phase with *MF*1 having the MW of 197 Da.

b. Photophysical properties of MFs 1-2 in different solvents.



Figure S5. Absorption spectra of MF1 (a) and MF2 (b) in different solvents.

Both these *MF*s exhibit two absorption bands in different solvents. The shorter wavelength band, ranging from 250 nm to 350 nm, is insensitive to polarity, whereas, the longer wavelength band, ranging from 350 nm to 520 nm, is sensitive to polarity. Thus, the shorter wavelength absorption band is assigned to be due to  $\pi$ - $\pi$ \* transition whereas the longer wavelength band is assigned to n- $\pi$ \* transition.



Figure S6. UV illuminated solution-phase pictures (a), emission spectra (b) and PL decay behaviour (c) of MF2 in different solvents. PL decays were monitored at the respective emission maximum, excitation wavelength is 405 nm.

For *MF*2, on changing the solvent polarity from hexane to acetonitrile (ACN), green (520 nm) to deep red (684 nm) emission has been observed. Single exponential PL decay has been observed for all solvents (hexane, mesitylene, toluene, benzene, dichloromethane (DCM) and ACN). Excited state lifetime initially increased from ~5 ns (hexane) to ~25 ns (benzene), and then decreased to ~1 ns (ACN) (see Table S3 for details).

Table S3. Photophysica	properties of MFs 1-2 is	n different solvents.
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MFs	Solvent	$\lambda_{abs}^{max}$ (n- $\pi^*$ ) (nm)	ε (*10 <sup>-3</sup> ) (M <sup>-1</sup> cm <sup>-1</sup> )	λ <sup>max</sup> (nm)	FWHM of PL emission (nm)	Solvatochromic shift (from hexane to ACN) (nm)	Stokes shift (nm)	Ф	τ (ns)
	Hexane	435	2.33	510	83		75	0.13	5.79
	Mesitylene	445	2.61	570	103		125	0.35	23.69
ME1	Toluene	448	2.32	578	105	104	130	0.45	22.72
MIT 1	Benzene	450	2.70	582	110	194	132	0.34	21.50
	DCM	454	2.75	625	127		171	0.19	11.84
	ACN	448	2.34	704	170		256	0.01	0.54
	Hexane	455	2.48	520	80		65	0.14	5.98
	Mesitylene	462	2.53	570	99		108	0.45	24.63
MED	Toluene	464	2.44	580	102	164	116	0.40	25.29
MIT 2	Benzene	465	2.57	588	105	104	123	0.44	25.40
	DCM	469	2.90	630	122		161	0.14	12.50
	ACN	466	2.26	684	151		218	0.01	1.62

#### c. Photophysical properties of para-fluorophores in different solvents.

Molecules	MW (Da)	Solvents	$\lambda_{abs}^{max}$ (nm)	λ <sup>max</sup> (nm)	Stokes shift (nm)	Solvatochromic shift (hexane/toluene to ACN) (nm)	Ф	τ (ps)
	107	Hexane	410	450	40	33	0.012	0.69
	197	ACN	419	483	64		0.014	1.40
EtO <sub>2</sub> C	244	Toluene	418	455	37	25	0.017	-
		ACN	421	480	59		0.023	-
MeO <sub>2</sub> C	201	Toluene	369	427	58	29	0.001	-
	291	ACN	374	456	82		0.001	-

Table S4. Photophysical properties of para-fluorophores (single pair of CTD and CTA moieties) with MW in the range of 197 to 291 Da.<sup>10-12</sup>

Excited state lifetimes of para-fluorophores with MW <250 Da are in the range of 600 femtosecond to 1.4 picosecond. However, in this article, we report excited state lifetime as high as 25 nanosecond. Thus, 20,000 times longer lifetime has been achieved in ultra-small MFs in comparison to para-fluorophores.

#### d. Photophysical properties of MFs 1-2 in solid state.



Figure S7. Crystal of *MF*1 in solid state under daylight (a), under UV–illumination (370 nm) (b), emission spectra (c) and PL decay behaviour (d) in mechanofluorochromic solid states of *MF*1. Solid state PL decays were obtained monitoring at the respective PL maximum, with the excitation wavelength of 405 nm.

Table S5. Photophysical properties of *MF*1 in solid states. PL decay has been monitored at the respective emission maximum. Excitation wavelength is 405 nm.

MF1	λ <sup>max</sup> (nm)	Ф	τ (ns)
Crystal	610	0.06	14.56
PMMA film	575	0.26	28.36
PS film	563	0.32	27.65

It is noteworthy to mention here that the PL emission maximum of para analogue of MF1 is 533 nm in solid state.<sup>11</sup> Thus, even in crystal the PL emission maximum of MF1 is much higher (77 nm) than the corresponding para-fluorophore.

Table S6. Photophysical properties of MF1 and MF2 in mechano-fluorochromic solid states. PL decay has been monitored at the respective emission maximum. Excitation wavelength is 405 nm.

	M	F1	MF2		
Sample	λ <sub>em</sub> (nm)	τ (ns)	λ <sub>em</sub> (nm)	τ (ns)	
Crystal	610	14.56	636	30.90	
Thin film	600	12.97	603	21.39	
10 min grinding	596	13.58	610	26.17	
60 min grinding	602	11.78	610	20.36	
After heating	606	10.81	610	19.01	
PMMA film	575	28.36	582	30.02	
PS film	563	27.65	568	33.09	

# e. Structural and photophysical properties of red emitting single benzene based fluorophore crystals with MW <400 Da.

**Table S7.** Photophysical properties of red emitting fluorophores having MW <400 Da and MFs 1-2 (in crystal).</th>

Chemical structure		MW (Da)	$\lambda_{em}^{max}$ (nm)	Φ	τ (ns)	Reference
	N	197	610	0.06	14.56	This work
	N CN	225	636	0.19	30.90	This work
R = NHMe	252	620	0.40	12.30	Angew. Chem. Int. Ed., 2017, <b>129</b> , 12717-12721	
R = NHEt	280	608	0.31	8.30	Angew. Chem. Int. Ed., 2017, <b>129</b> , 12717-12721	
	290	620	0.04	7.42	Chem. Sci., 2017, <b>8</b> , 577-582	
R = NHiPr		308	618	0.39	11.80	Angew. Chem. Int. Ed., 2017, <b>129</b> , 12717-12721
HO HN CO <sub>2</sub> Me	Polymorph A	320	622	0.08	6.10	J. Phys. Chem. Lett., 2019, 10,
MeO <sub>2</sub> C' V NH	Polymorph B	320	640	<0.01	-	1437-1442

As shown above, in crystal, red emission has been reported with fluorophores having lowest MW of 252 Da. In this article, we are reporting red emission in crystal with an ultra-small MF with MW of only 197 Da. Highest excited state lifetime for red emitting crystal has so far been reported to be 12.30 ns, however, in this article we report the longest excited state lifetime of 30.90 ns.

f. Powder XRD, IR and DSC of MFs 1-2.



Figure S8. Powder X-ray diffraction (XRD) patterns of *MF*1 (a) and *MF*2 (b) based on the single-crystal structures (simulated) and the measured XRD pattern of the powdered sample after grinding for different time durations.



Figure S9. CN stretching frequency of crystal, after grinding with different grinding time and after heating of MF1 (a) and MF2 (b).



**Figure S10.** DSC of *MF*1 (a) and *MF*2 (b).

#### g. Nanoindentation : mechanical properties of MFs 1-2.

Indentation experiment was possible only on (001) face of the MF1 and MF2 single crystals as other faces were not accessible. For both the crystals, force was applied by the indenter parallel to the layer-like architectures. During loading of the tip inside the samples, there was gliding of layers which allows easy movement of the tip resulting in significant plastic deformation.

The magnitudes of Young's modulus (*E*) and hardness (*H*) which exhibit the ability of a material to resist against elastic and plastic deformation respectively, have been extracted from the experimental *P*-*h* (load-depth) curves following Oliver-Pharr method,<sup>5</sup> from small volume of material of very tiny crystal faces using sharp berkovich tip (radius ~150 nm). Load displacement (*P*-*h*) curves on both crystals show large residual depths upon unloading, which confirms the soft nature of both the crystals. The loading curves exhibit several displacement bursts (often termed as 'pop-ins' in the indentation literature), indicating intermittent plastic flow. The magnitude of *H* for both *MF*1 and *MF*2 crystals show similar resistance against the plastic deformation for both the crystals. Slightly higher value of *E* for the *MF*1 signifies marginally stiffer nature of the *MF*1 crystal in comparison to *MF*2.



Figure S11. Load-depth curve from nanoindentation (a), layer like packing for structures of MF1 (b) and MF2 (c).

**Table S8.** Mechanical properties of crystals of *MF*1 and *MF*2.

Crystal	Young's Modulus (E) (GPa)	Hardness (H) (GPa)		
MF1	$5.50 \pm 0.30$	$0.24 \pm 0.02$		
MF2	$5.36 \pm 0.14$	$0.24 \pm 0.01$		

#### h. Comparison of optical properties of MFs 1-2 in crystal.

**Table S9.** Optical properties of *MF*1 and *MF*2 in crystal.

Crystal	Crystal system	λ <sub>em</sub> (nm)	FWHM of PL (nm)	Ф	τ (ns)
MF1	Monoclinic	610	85	0.06	14.56
MF2	Triclinic	636	76	0.19	30.90

# i. Crystal structure analyses of MFs 1-2.

 Table S10. Crystallographic data of MFs 1-2.

Crystal parameters	MF1	MF2
Formula	C <sub>12</sub> H <sub>11</sub> N <sub>3</sub>	C <sub>14</sub> H <sub>15</sub> N <sub>3</sub>
Crystal system	Monoclinic	Triclinic
Space group	P2 <sub>1</sub> /c	PĪ
a (Å)	15.292(4)	8.7161 (6)
b (Å)	10.450(3)	9.2511 (7)
c (Å)	6.872(2)	9.8844 (7)
α (°)	90	63.309 (8)
β (°)	97.614(10)	64.432 (7)
γ (°)	90	72.772 (7)
V (Å <sup>3</sup> )	1088.5	637.16
Ζ	4	2
Z'	2	1
Т	301	293
μ [mm <sup>-1</sup> ]	0.075	0.561
R	0.1058	0.0782
wR <sub>2</sub>	0.2667	0.2367
GOOF	1.126	1.125
CCDC number	2042111	2017383

**Table S11.** Different kind of interactions of crystal MFs 1-2 with bond distances and angles.

MFs	Bonds	Interactions	Bond distance (Å)	Angle (°)
ME1	C1-H1…N3	Intra-molecular	2.68	151.71
MIT 1	C12-H12…N3	Inter-molecular	2.61	174.55
MED	C1-H1…N3	Intra-molecular	2.65	152.00
MF2	C7-H7…N2	Inter-molecular	2.68	164.64

¢-¢-¢-		c
Parameters	MF1	MF2
$d(\text{\AA})$	3.65	3.59
θ (°)	152.91	164.72

Figure S12. Distinction of strength of the hydrogen bond of *MF*1 and *MF*2 crystals.

#### j. Energy frameworks calculations of MFs 1-2.

Interaction energies were calculated at B3LYP/6-31G(d,p) level of theory using Crystal Explorer 17.5 software.<sup>13</sup> Energy frameworks and different types of interaction energies along different directions for MF1 (Figure S13-S17) and MF2 (Figure S18-S22) are designated below.



Figure S13. Crystal explorer-based energy frameworks and magnitudes of different types of interaction energies for the *MF*1 crystal, with a 100 energy scale factor and a zero energy threshold.



Figure S14. Crystal explorer-based energy framework (a) and the table (b) depicting the energy values (in kJ/mole) for the MF1 crystal, with a 100 energy scale factor and a zero energy threshold.



Figure S15. Crystal explorer-based energy framework (side view, showing the central molecule in black colour) for the MF1 crystal, with a 100 energy scale factor and a zero energy threshold.



Figure S16. Crystal explorer-based energy frameworks, different types of interaction energies along the direction of intermolecular hydrogen-bond for the *MF*1 crystals with a 100 energy scale factor and a zero energy threshold.



Figure S17. Crystal explorer-based energy framework (a) and the table (b) depicting the energy values (in kJ/mole), along the direction of intermolecular hydrogen-bond for the *MF*1 crystal, with a 100 energy scale factor and a zero energy threshold.



Figure S18. Crystal explorer-based energy frameworks and magnitudes of different types of interaction energies for the MF2 crystal with a 100 energy scale factor and a zero energy threshold.



Figure S19. Crystal explorer-based energy framework (a) and the table (b) depicting the energy values (in kJ/mole), for the MF2 crystal with a 100 energy scale factor and a zero energy threshold.



Figure S20. Crystal explorer-based energy framework (side view, showing the central molecule in black colour) for the MF2 crystal with a 100 energy scale factor and a zero energy threshold.



Figure S21. Crystal explorer-based energy frameworks, different types of interaction energies along the direction of intermolecular hydrogen-bond for the *MF*2 crystals with a 100 energy scale factor and a zero energy threshold.



Figure S22. Crystal explorer-based energy framework and the table (b) depicting the energy values (in kJ/mole), along the direction of intermolecular hydrogen-bond for the *MF*2 crystal with a 100 energy scale factor and a zero energy threshold.

Table S12. Different types of interaction energies of MFs 1-2 in crystals.

		Entire crystal	
Molecule	Coulomb energy (kJ/mol)	Dispersion energy (kJ/mol)	Total energy (kJ/mol)
MF1	-77.4	-215.6	-202.9
MF2	-66.7	-218.3	-201.9

MF2 crystals are softer than MF1 due to presence of weaker van der Waals interaction and from pairwise energy calculations also it reveals that the magnitude of dispersion energy is more for MF2 (-218.3 kJ/mol) than that for MF1 (-215.6 kJ/mol). MF1 is marginally stiffer than MF2 due to 1D hydrogen-bonded chain, as MF1 has more Coulomb energy (-77.4 kJ/mol) than MF2 (-66.7 kJ/mol).

#### k. Hirshfeld surface analysis and percentage of interactions of MFs 1-2.

Important intermolecular interactions (Figure S23 and S24) within the crystal structure of *MF*1 and *MF*2, respectively, were identified through Hirshfeld surface analysis using Crystal Explorer 17.5.<sup>13</sup> The Hirshfeld surface is defined as a set of points in 3D space where the ratio of promolecule and procrystal electron densities equals 0.5.<sup>14</sup> The exploration of intermolecular contacts is provided by mapping normalized contact distances ( $d_{norm}$ ), which is a function of the closest distance from the point to the nuclei interior ( $d_i$ ) and exterior ( $d_e$ ) to the surface as well as on the van der Waals radii ( $r_{vdw}$ ). The percentage of interactions obtained from the Hirshfeld surface analysis is visualized in the following pi-chart (Figure S25 and S26) for *MF*1 and *MF*2, respectively.



Figure S23. Hirshfeld surface in the crystal structure of MF1 along different orientations (a-c).



Figure S24. Hirshfeld surface in the crystal structure of MF2 along different orientations (a-c).



Figure S25. Pi-chart showing the percentage of interactions obtained from the Hirshfeld surface analysis in the crystal structure of MF1.



Figure S26. Pi-chart showing the percentage of interactions obtained from the Hirshfeld surface analysis in the crystal structure of MF2.

Table S13. Results of the Hirshfeld surface analysis for stronger interactions in crystals of MFs 1-2.

d (adjacent to the C atom)	d	Interactions (%)		
di (aujacent to the C atom)	u <sub>e</sub>	MF1	MF2	
Ci	Ce	16.3	7.2	
Hi	Ne	15.0	12.1	
Ni	He	19.1	15.7	

#### I. Non-covalent interaction (NCI) calculations of MFs 1-2.

Non-covelent interaction (NCI) calculations of MFs have been performed by using multifunctional wave function analyzer (Multiwfn)<sup>15</sup> and visual molecular dynamics (VMD)<sup>16</sup> programes. The crystal geometries of the MFs have been used for these calculations. Moreover, to get insight into the existence and degree of extension of NCIs in the crystal state, reduced density gradient iso-surface and reduced density gradient (RDG) scattering plot have been studied for both the monomer and the dimer of both MFs. The green spikes in the RDG scatter plot where the presence of electron density is almost zero, indicate the presence of van der Waals interactions (vdWs). Blue dots the RDG scatter diagram indicate the strong attraction and red dots in the RDG scatter diagram indicate strong repulsion.



**Figure S27.** The reduced density gradient iso-surface (a,c) and plot of the reduced density gradient (RDG) versus  $sign(\lambda_2)\rho$  (b,d) of the monomer for *MF*1 (upper row) and *MF*2 (bottom row) crystals.



#### m. Computational calculations of MFs 1-2.

Figure S28. Geometry optimized structures and HOMO, LUMO (a) and energy gap (HOMO-LUMO) of MFs 1-2 (b).

Computational calculation shows that in the HOMO, there is very significant electronic charge density on nitrogen (of NR<sub>2</sub> charge-transferdonor (CTD) group), but, there is no electronic charge density on acceptor. Whereas, in the LUMO there is nearly no charge density on the nitrogen (of NR<sub>2</sub> CTD group), but there is significant charge density on the acceptor moiety. These observations hint towards very significant charge transfer in both MF1 and MF2.



Figure S29. Computationally (gas phase) obtained energies of conformer 1, 2 and transition state energy barrier of MF1 (a) and MF2 (b).

Table S14. Ext	perimentally	(hexane).	and comp	utationally	(gas	phase)	obtained a	bsorption	maxima and	correspondi	ng oscillator	strength	of MFs 1	1-2.
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MFs	μ <sub>g</sub> (D)	μ <sub>e</sub> (D)	Δμ (D)	$\lambda_{abs}^{max}$ (experimental, hexane) (nm)	$\lambda_{abs}^{max}$ (Computational, gas phase) ( <b>nm</b> )	Oscillator strength
MF1	9.18	21.98	12.80	435	470	0.0299
MF2	9.50	22.49	12.99	455	480	0.0210

Table S15. Comparison of experimentally (hexane) obtained absorption energy with the computationally (gas phase) obtained absorption energy (both conformer 1 and 2).

	Experimental results (hexane)	Computational results (gas phase)				
MFs	λ <sup>max</sup> abs (nm)	Conformer 1 $\lambda_{abs}^{max}$ (nm)	Conformer 2 $\lambda_{abs}^{max}$ (nm)			
MF1	435	470	487			
MF2	455	481	499			

#### n. Experimental and computational analyses for CT-mediated J-aggregation of MFs 1-2.

Density functional theory (DFT) was used to optimize the monomers using the CAM-B3LYP exchange correlation functional and the 6-31G(d,p) basis set in Gaussian09.<sup>17</sup> The overlap integrals of HOMO-HOMO and LUMO-LUMO between the two monomers in the dimer of *MF*s were obtained by Multiwfn program.<sup>15</sup> The charge-transfer (CT) is a method derived based on hole-electron analysis for quantitatively studying amount of CT between different fragments. The orientation of transition dipole moments (TDMs) contributed by molecular fragments was plotted using multifunctional wave function analyzer (Multiwfn)<sup>15</sup> and visual molecular dynamics (VMD)<sup>16</sup> programs. The optimizations of *MF*1 and *MF*2 dimers have been carried out using wB97XD exchange correlation functional and 6-31G(d,p) basis set. The splitting energy of exciton states in dimer with inclined packing motifs has been calculated by using the following equation (*eq.* 4):

Exciton splitting energy = 
$$\frac{2|M|^2}{d_{c-c}^3} (1 - 3\cos^2\theta) \dots \dots \dots eq.4$$

where M is the transition dipole moment of pristine exciton state,  $d_{c-c}$  is the intermolecular center-to-center distance, and  $\theta$  is the slip angle of the dimer.

Table S16. Comparison (our work and literature reports) of experimentally and computationally calculated parameters for the evidence of CT-mediated J-aggregation.

Sl. No.	Compound name (as mentioned in references)	CT amount	Solvato- chromic shift (nm)	Perpendi- cular distance (Å)	Slip angle (°)	Angle between TDM (°)	Exciton splitting energy (meV)	HOMO- HOMO overlap integral	LUMO- LUMO overlap integral	ΔEes (eV)	τ (ns)	Ref. No.
1	MF2	0.82	164	3.40	44.05	66.99	-55.7	0.0068	-0.00024	0.83	30.90	Our work
2	СМОА	0.54	~50	3.4	88.2	NR	-1200	-0.0097	-0.0122	1.36	NR	18
3	SQ3	NR	NR	3.33, 3.35	87, 27	NR	NR	NR	NR	0.37	NR	19
4	SQ4	NR	NR	3.38	29	NR	NR	NR	NR	0.50	NR	20
5	SQ1	NR	NR	3.46	NR	31.1	NR	NR	NR	0.61	NR	21
6	DPrSQ(OH)2	NR	NR	3.3	NR	NR	NR	NR	NR	0.51	NR	22
7	DBSQ(OH)2	NR	NR	3.3	NR	NR	NR	NR	NR	0.44	NR	22
8	BDP2	NR	NR	2.63, 2.65	NR	NR	NR	NR	NR	0.30	2.79	22
9	BDP3	NR	NR	3.44, 3.73	NR	NR	NR	NR	NR	0.35	2.07	23

\*NR = Not reported



**Figure S30.** Reduced density gradient (RDG) iso-surface (a), and plot of the RDG versus sign( $\lambda_2$ ) $\rho$  (b) of the dimer, molecular packing structures (c) derived from the single-crystal structure, where computationally derived  $\pi$ - $\pi$  stacked slip angle ( $\alpha$ ) between S<sub>0</sub> to S<sub>1</sub> transitional dipole moment (TDM) has been shown (TDM directions are indicated in a green arrow), calculated HOMO–HOMO and LUMO–LUMO overlaps of a representative dimer (d), experimentally derived  $\pi$ - $\pi$  stacked slip angle from the crystal packing (e), and comparison of absorption (f), excitation (g) and excited state lifetime (h) in hexane, thin film and crystal, for the *MF*1 crystal.

Table S17. Experimentally and computationally calculated parameters for the evidence of CT-mediated J-aggregation for MF1 crystal.

Compound	CT amount	Solvato- chromic shift (nm)	Perpendi- cular distance (Å)	Slip angle (°)	Angle between TDM (°)	Exciton splitting energy (meV)	HOMO- HOMO overlap integral	LUMO- LUMO overlap integral	ΔEes (eV)	τ (ns)
MF1	0.82	194	3.44	44.15	109.08	-10.5	-0.01487	0.00819	0.82	14.56

The magnitudes of CT coupling constant ( $J_{CT}$ ) and Coulomb coupling constant ( $J_{Coulomb}$ ) have been calculated according to the following equations:<sup>24</sup>

$$J_{CT} = \frac{-2D_e D_h}{E_{CT} - E_{S_1}} \dots \dots \dots \dots eq.5$$

where  $D_e$  = electron dissociation integrals,  $D_h$  = hole dissociation integrals,  $E_{CT}$  = energy of the CT state,  $E_{S_1}$  = energy of S<sub>1</sub> state.

$$J_{Coulomb} = \frac{M^2(1 - 3\cos^2\theta)}{4\pi\epsilon R^2} \dots \dots \dots eq.6$$

where M = transition dipole moment vector,  $\theta$  = the angle between the transition dipole moment vector M and the line connecting the molecular centers, i.e. the slip angle,  $\varepsilon$  = dielectric constant of the medium, R = perpendicular interplanar distance.

The estimated magnitudes of J<sub>CT</sub> and J<sub>Coulomb</sub> are -0.6296, 0.0028 (for MF1) and -0.7083, 0.0155 (for MF2).

#### o. LED applications of MFs 1-2.

#### Yellow LED generation:

In a glass vial, *MF* dissolved in toluene was mixed in a saturated toluene solution of polystyrene (PS). This *MF*-PS mixture was coated uniformly on a commercially available UV-LED (365-395 nm) followed by drying in air to make a yellow emitting LED. The resulting yellow emission was optically characterized by PL spectroscopy with CIE chromaticity coordinates and CCT values.

#### White LED generation:

The *MF*-PS mixture was coated uniformly on a commercially available Blue-LED (400-500 nm) followed by drying in air. The resulting white emission was optically characterized by PL spectroscopy with CIE chromaticity coordinates and CCT values.



Figure S31. Yellow and white LEDs (a,d), corresponding emission spectral profile of yellow and white LEDs (b,e) and CIE chromaticity coordinates of yellow and white LEDs (c,f), respectively, for MF1.



Figure S32. Yellow and white LEDs (a,d), corresponding emission spectral profile of yellow and white LEDs (b,e) and CIE chromaticity coordinates of yellow and white LEDs (c,f), respectively, for *MF*2.

Table S18. CIE coordinates and CCT values for colour pr	re yellow and white LEDs generat	ed from both MF1 and MF2.
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Parameters	M	F1	MF2			
	Yellow LED	White LED	Yellow LED	White LED		
CIE coordinates	<b>CIE coordinates</b> (0.46, 0.52)		(0.47, 0.51)	(0.32, 0.34)		
CCT value (K)	3393	6740	3215	6073		

#### p. Stability of yellow and white LEDs generated from MFs 1-2.



Figure S33. Stability of yellow and white LEDs employing MF1 (a and b respectively) and MF2 (c and d respectively).

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