Supporting Information

An Unusual Non-Emissive Behaviour of Rubrene J-Aggregates: a Rare Violation

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Table S1: The optical signatures of RB monomer and RB J-aggregate obtained via steady state UV-vis absorption spectroscopy.

	Absorption wavelength, λ (nm)	ε_{max} ($L.mol^{-1}.cm^{-1}$)	FWHM (cm^{-1})	Area under the absorption band, $\int \varepsilon . d\bar{\nu}$,	Oscillator strength, f = $4.32 \times 10^{-9} \int \varepsilon . d\bar{\nu}$	Transition Dipole Moment, $\vec{M}$ (D) = $0.461 \times \sqrt{f \times \lambda \text{ (nm)}}$
RB Monomer	526	6616.2	1042	7345241.4	0.032	1.88
RB J-Aggregate	531	6099.7	1073	6651214.7	0.029	1.80

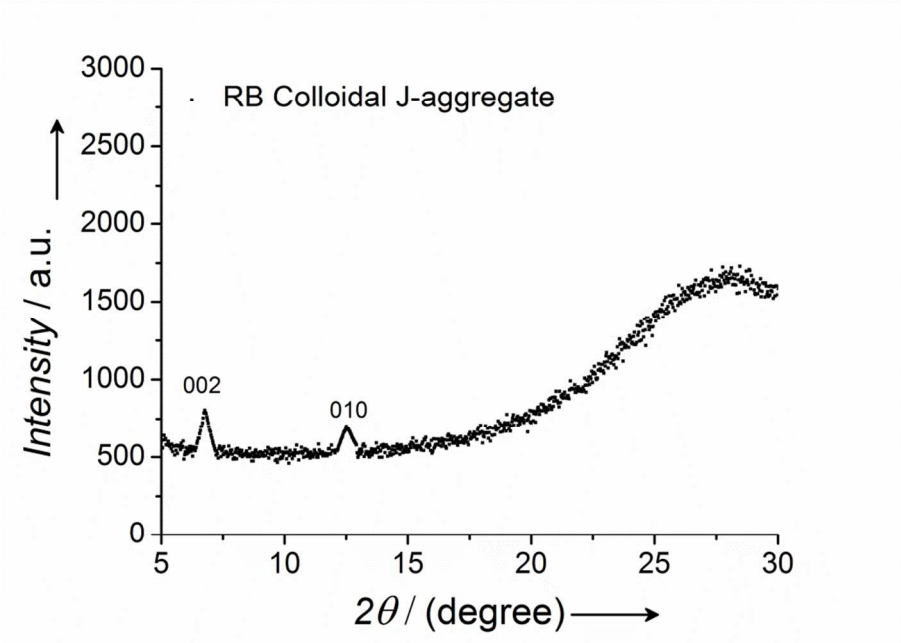

Figure S1. XRD patterns of as-prepared spherical RB colloidal J-aggregates in THF-Water binary (water volume fraction = 0.97) mixture resembling the rhombic crystal lattice.

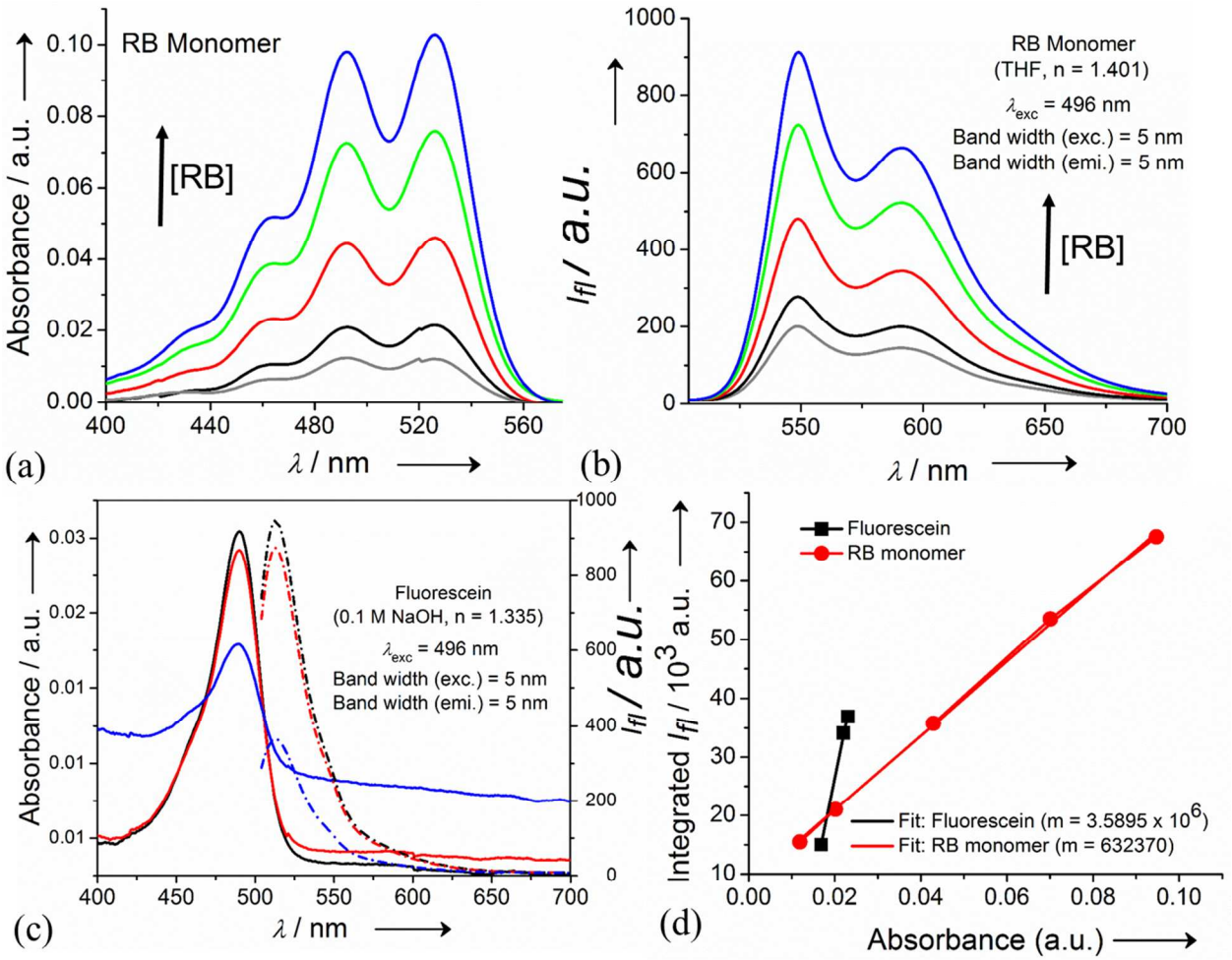

Figure S2 (a) and (b) UV-vis absorption and corresponding emission spectra of RB monomer in THF for estimation of PL quantum yield. (c) UV-vis absorption and corresponding emission spectra of Fluorescein standard in different concentrations in 0.1 M NaOH solution. (d) The integrated fluorescence intensity vs. absorbance of RB monomer and Fluorescein obtained from (a), (b) and (c), following a straight line equation with their corresponding slopes 'm'.

$$\phi_{mon} = \frac{m_{mon} \cdot n_{THF}}{m_{fluo} \cdot n_{NaOH\ (0.1M)}} \phi_{fluo} = \frac{632370}{3589500} \frac{1.407}{1.335} 0.925 = 0.172$$

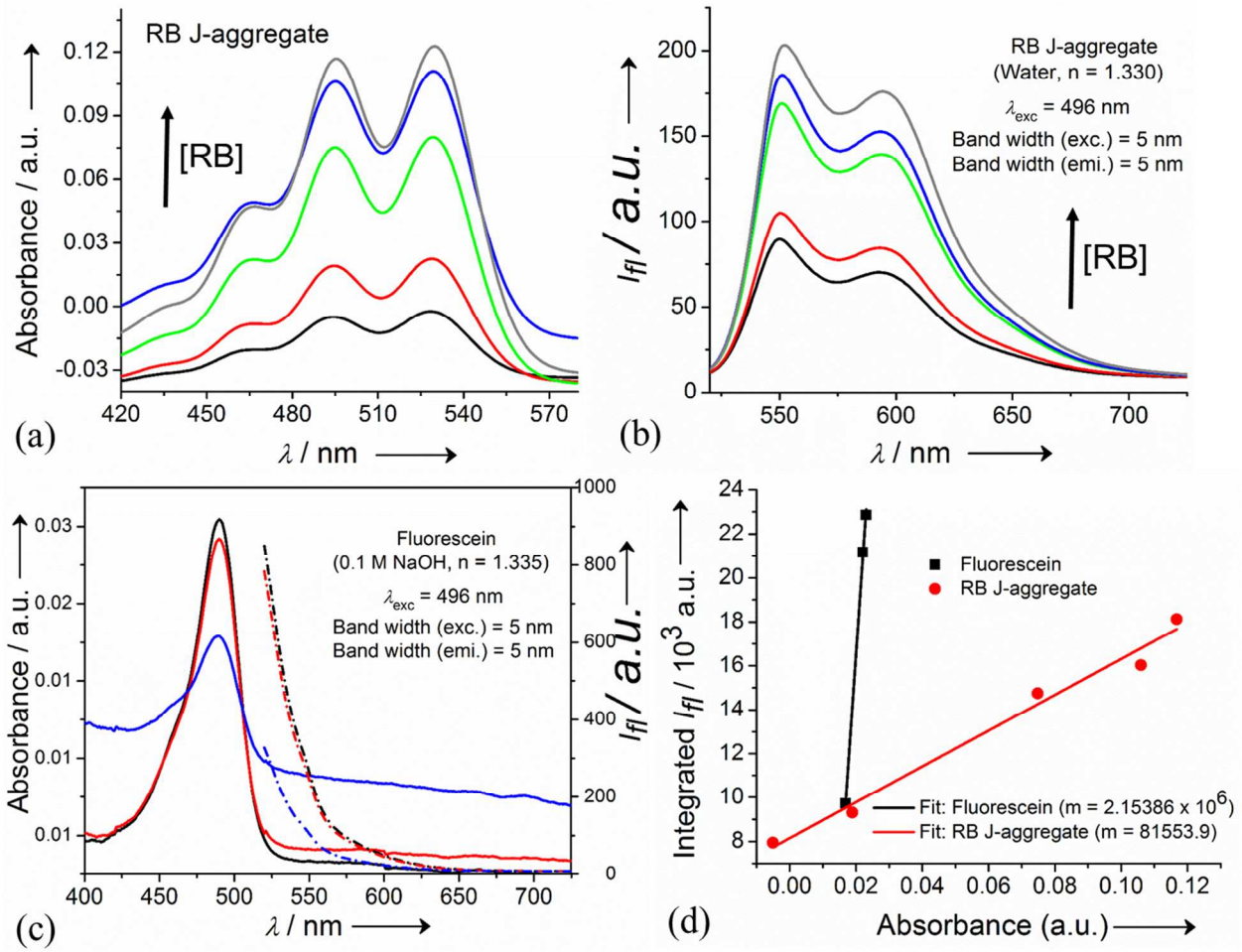

Figure S3 (a) and (b) UV-vis absorption and corresponding emission spectra of RB J-aggregate in THF: water binary mixture (f_w = 0.97) for photoluminescence quantum yield calculation. (c) UV-vis absorption and corresponding emission spectra of Fluorescein reference in different concentrations in 0.1 M NaOH solution. (d) The integrated fluorescence intensity vs. absorbance of RB J-aggregates and Fluorescein obtained from (a), (b) and (c), following a straight line equation with corresponding slopes 'm'.

$$\phi_{agg} = \frac{m_{agg} \cdot n_{water}}{m_{fluo} \cdot n_{NaOH\ (0.1\ M)}} \phi_{fluo} = \frac{81553.9}{2153860} \frac{1.330}{1.335} 0.925 = 0.035$$

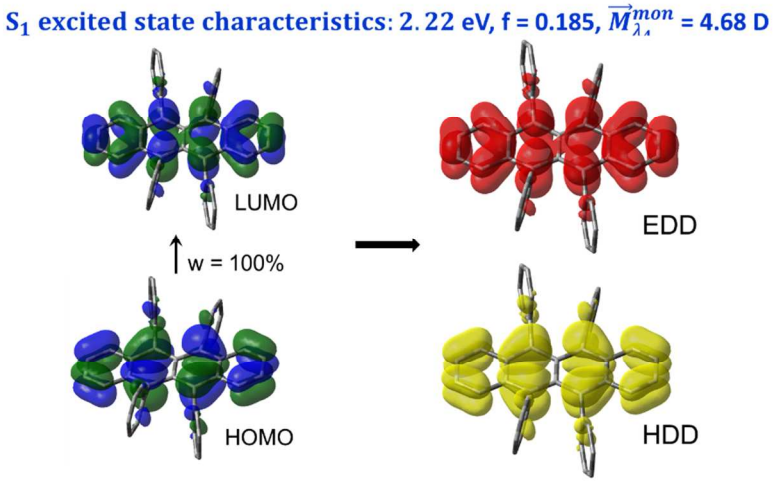

Figure S4. Associated molecular orbitals, the oscillator strength and the weight of the 2.22 eV transition of the RB monomer, computed via TD-DFT-B3LYP/6-31G+(d,p) level with IEFPCM in THF. Electron (EDD) and hole (HDD) density distribution maps associated with the monomer excited state corresponding to 2.22 eV electronic transition.

Table S2: Computed Centroid Coordinates of EDD and HDD for S_1 Excited State of RB Monomer.

RB monomer (S_1 excited state)	Centroid Coordinates		
	X (Å)	Y (Å)	Z (Å)
EDD	0.211	-0.097	0.0131
HDD	-0.379	-0.025	0.0126

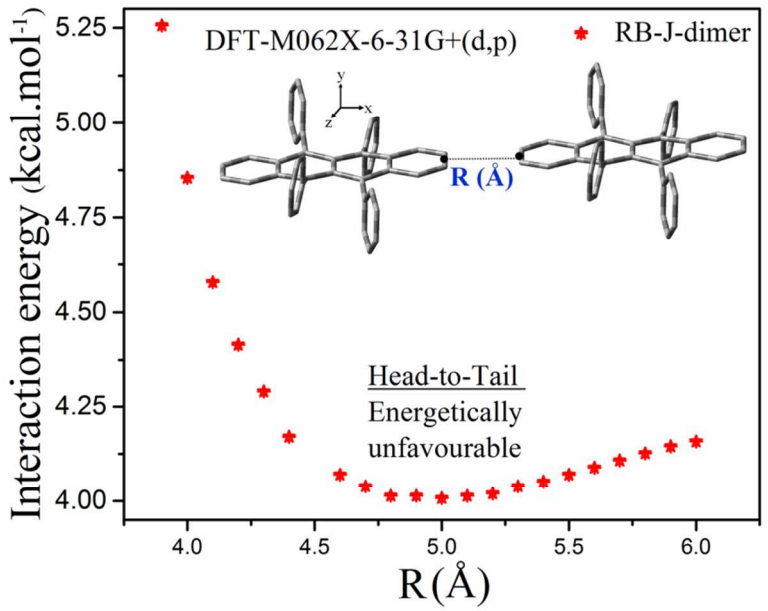

Figure S5. The equilibrium positive interaction energy on the computed potential energy curve discards the formation of a Rubrene ideal J-dimer ($\theta = 0^{o}$).

Table S3: Computed indexes towards characterization of low lying dark and bright singlet states in Rubrene J-dimer.

Excited state	Energy (eV)	Oscillator strength	$\varphi_{C^+C^-}$	t-index			Character
				x (Å)	y (Å)	z (Å)	
S_1	2.53	0.283	0.959	-1.94	-4.61	-1.45	LE
S_2	2.55	0.000	0.957	-1.981	-4.67	-1.45	LE
S_3	3.08	0.000	0.957	-1.97	-4.72	-1.46	LE
S_4	3.14	0.047	0.955	-1.97	-4.67	-1.47	LE
S_5	3.54	0.000	0.825	-1.86	-4.17	-2.28	LE
S_6	3.56	0.000	0.767	-1.928	-4.29	-2.28	LE