Supporting Information

Charge Transfer-Induced Assembly of a Gold Nanocomposite Mediated by N-methylfulleropyrrolidine: Excitation Energy Transfer from Rhodamine B

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^{1}H-NMR spectrum of 8-NMFP: Multiplet peaks observed for both $–CH_2$ (m, 32H) and $–CH_3$ (m, 24H) at 3.50 ppm and 2.56 ppm respectively due to presence of H of $–CH_2$ and $–CH_3$.

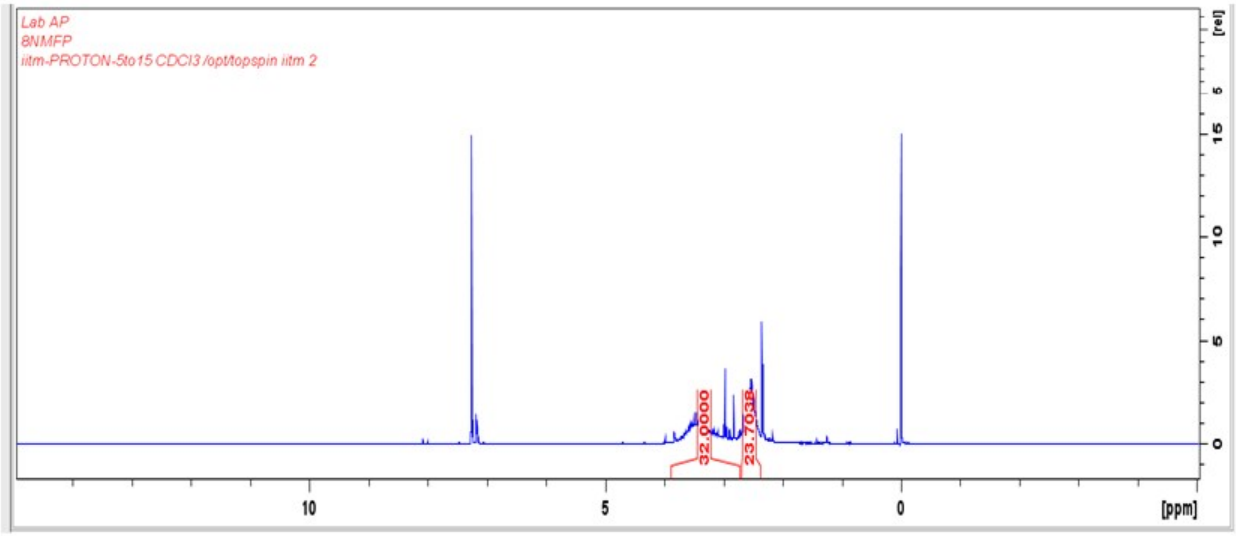

Fig. S1 ^{1}H-NMR spectrum of 8-NMFP.

MLADI-TOF of 8-NMFP: MALDI mass (M^+) = 1177.65 amu, calculated mass = 1177.39 amu

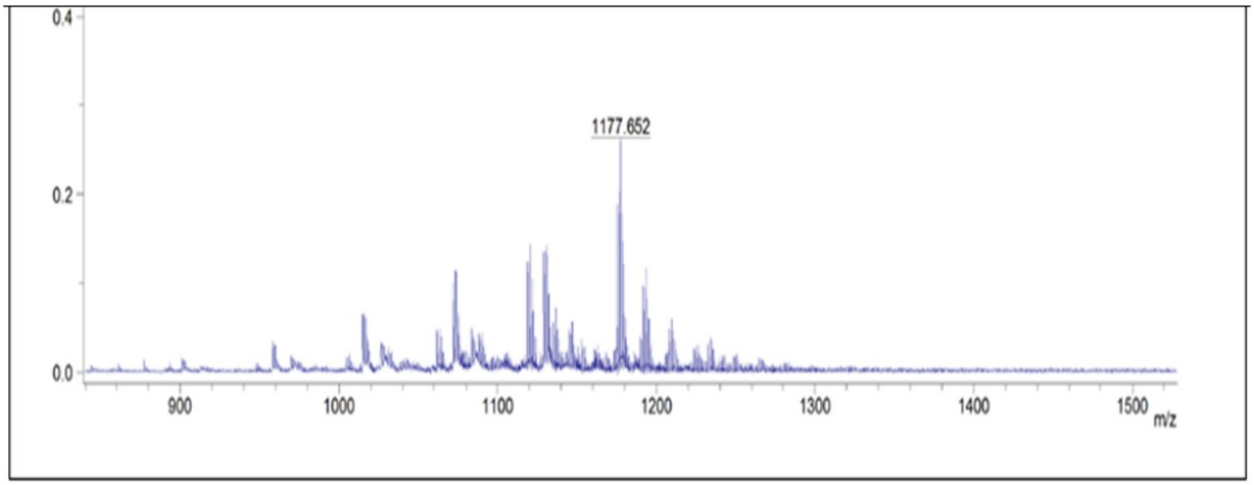

Fig. S2 MALDI-TOF of 8-NMFP showing the molecular ion peak

Integration of ^{1}H-NMR peaks and MALDI mass proved for presence of eight number of pyrrolidine moieties attached onto fullerene surface.

UV-visible spectra of 8-NMFP and citrate and 3-MPA Capped gold NPs: UV-visible absorption feature for 8-NMFP shows a strong peak at 260 nm. The characteristic peaks of fullerene-C_{60} (410 - 620 nm due to orbital forbidden singlet-singlet transitions) [1] are weak and hardly visible. Surface plasmon resonance (SPR) peak is seen for Ct@Au and mpa@Au at ~ 520 and 522 nm respectively. A red shift (2 nm) is due to ligand place exchange reaction with 3-MPA ligand.

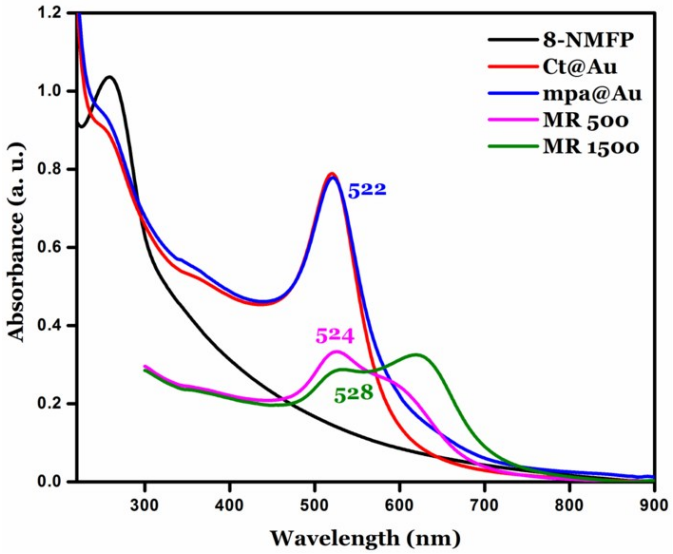

Fig. S3 UV-visible spectra of 8-NMFP, Ct@Au, mpa@Au NPs and MR of 500 and 1500 (at 45 min)

IR spectra of 8-NMFP and citrate and 3-MPA capped gold NPs: The IR spectra of fullerene C_{60} and 8-NMFP are shown in figure S7 (a). Of 74 vibrational modes of C_{60} only 42 are fundamentals of various symmetries. Again, out of 42 fundamentals only four have t_{1u} symmetry and are IR active. [2] These 4 modes of C_{60} are seen at 521, 575, 1176 and 1430 cm^{-1}. For 8-NMFP, along with the two higher wavenumber C_{60} bands 2933, 2768 cm^{-1} features are attributed to the C-H (both $-CH_3$ and $–CH_2$) stretching. The band at 1335 cm^{-1} is due to C-N bond stretching. In the IR-spectra of 3-MPA and 3-MPA capped gold NPs, the vibrational frequency due to –SH at 2560 cm^{-1} is absent in 3-MPA capped gold NPs. The vibrational frequencies due to –C=O and –C-O of –COOH are shifted to lower frequencies (1630 and 1394 cm^{-1}) as a result of attachment of –S to the gold core.

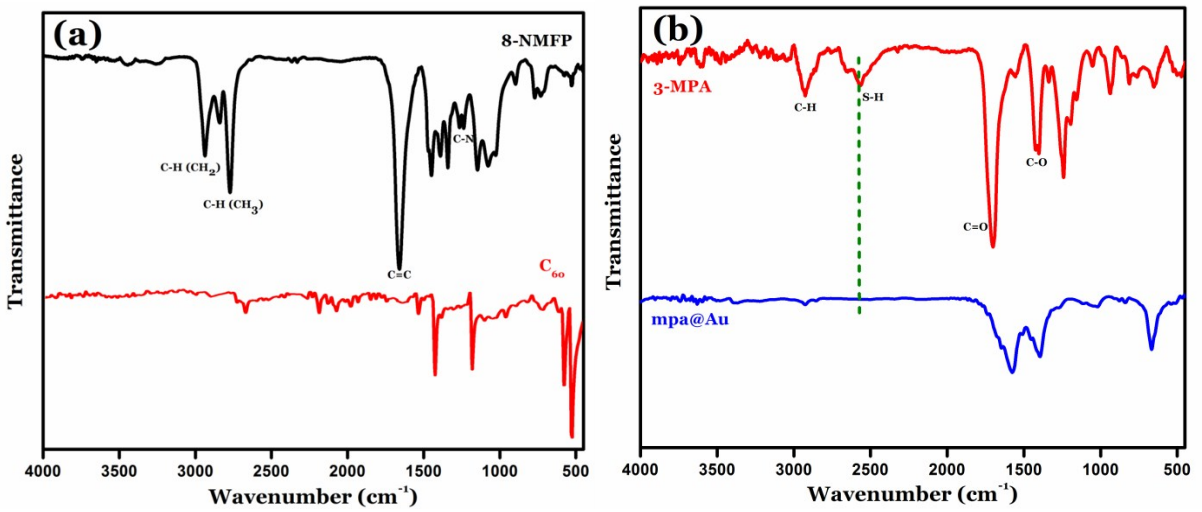

Fig. S4 (a) IR spectra of 8-NMFP and fullerene-C_{60}. (b) IR spectra of 3-MPA and 3-MPA capped gold NPs.

Calculation of concentration of 3-MPA capped gold NPs:

Using the UV-Vis spectral characteristics and the size of the NPs from TEM, the concentration of mpa@Au NPs was estimated as follows, following the reference 3:

The absorbance ratio as absorbance at the surface plasmon resonance band (522 nm) divided by the absorbance at 450 nm (base absorbance of the surface plasmon band) was first estimated.

Absorbance ratio = A_{spr}/A_{450} = 0.778 / 0.464 = 1.68, which corresponds to size ~18 nm as found from TEM, further corresponds to the ε value ~3.87 x 10^8 $M^{-1}cm^{-1}$ [3]

Hence, concentration of mpa@Au NPs = $A_{450}/\varepsilon_{450}$ = 0.464 / 3.87 x 10^8 = 1.20 nM

Preparation of the composite:

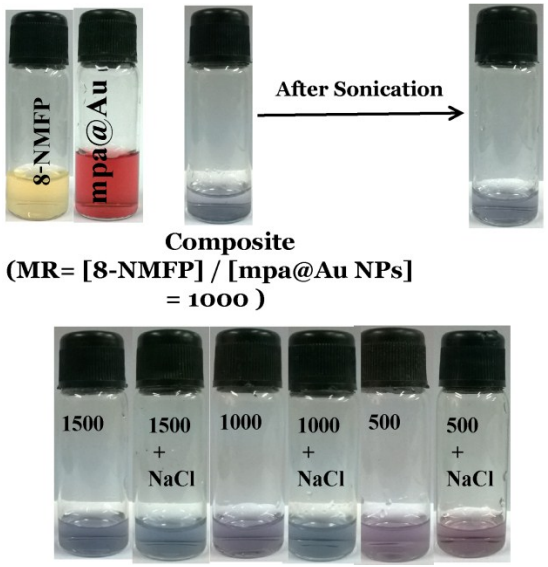

Fig. S5 Digital photographs of the prepared composite synthesized from different MRs in presence and absence of NaCl.

Spectral evolution with different MRs:

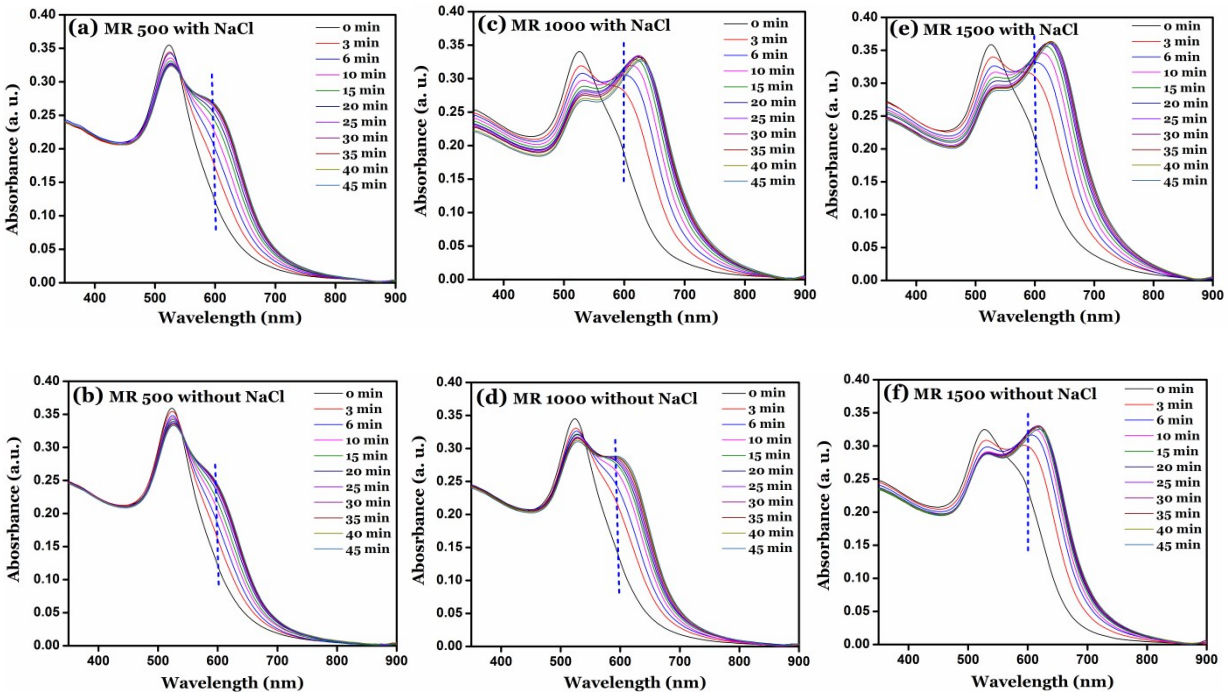

Fig. S6 Spectral evolution of 8-NMFP mediated assembly with MR 500 (a = with NaCl, b = without NaCl), 1000 (c = with NaCl, d = without NaCl) and 1500 (e = with NaCl, f =without NaCl

Kinetic plots for the composite formation with respect to different MR:

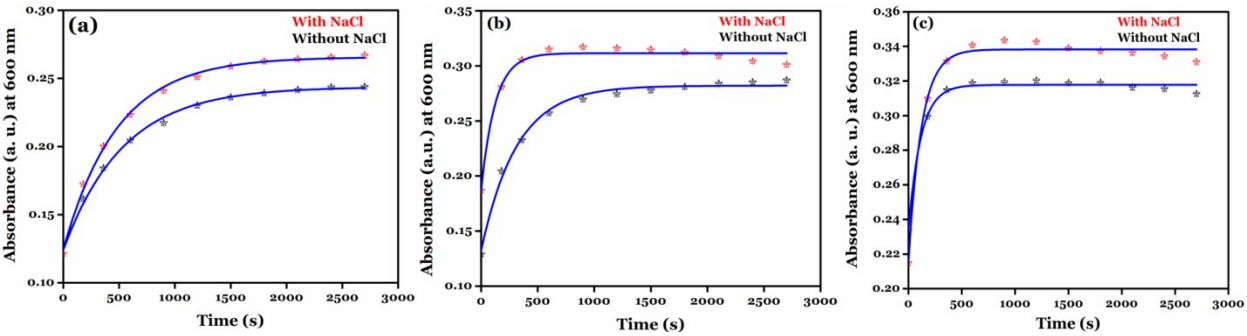

Fig. S7 Temporal evolution of the ~600 nm feature in the UV-visible kinetic plots for MR 500 (a), 1000 (b) and 1500 (c).

Table S1: Apparent rate constants for the composite assembly corresponding to MR 500, 1000 and 1500 with and without NaCl.

MR ([8-NMFP]/[mpa@Au])	Rate constant (s^{-1}) with NaCl	Rate constant (s^{-1}) without NaCl
500	2.07×10^{-3}	1.87×10^{-3}
1000	8.01×10^{-3}	3.18×10^{-3}
1500	8.68×10^{-3}	8.23×10^{-3}

TEM micrographs for pH dependent study:

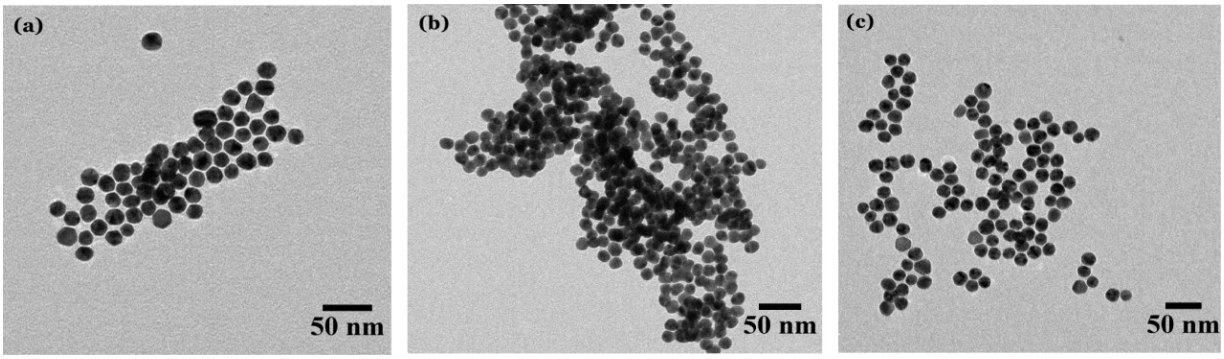

Fig. S8 TEM micrographs at pH 2.5 (a), 6.8 (b) and 9.0 (c) respectively with MR 350.

Apparent hydrodynamic diameter of the composite with and without electrolyte:

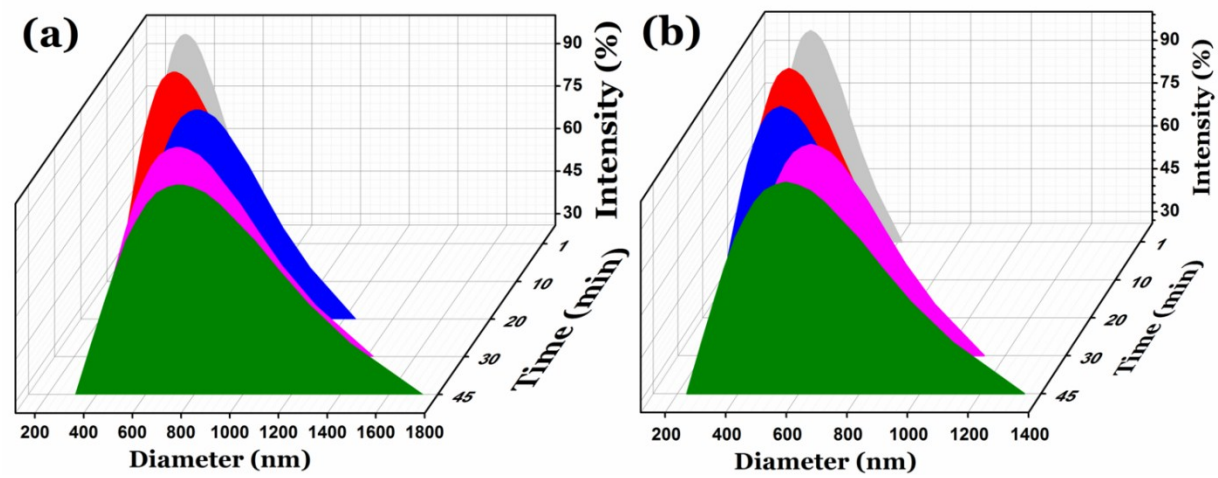

Fig. S9 Dynamic light scattering profiles with NaCl (a) and without NaCl (b).

Computation of 3-MPA and 8-NMFP: The ground state geometry (energy -684.31 a.u.) and ESP map of 3-MPA shown in Fig. S10 a and b and estimate its area to be 19.04 $Å^2$ (0.19 nm^2) with maximum electron density over the more electronegative O and S atoms. The input geometry for 8-NMFP optimization was taken with the first six moieties of pyrrolidine attached to six pyracylene units of fullerene-C_{60} (as an octahedral geometry). The rest two pyrrolidine moieties were attached next to opposite of any two pyrrolidine moieties at 6:6 position of fullerene-C_{60}. The ground state geometry of 8-NMFP was thus optimized with an estimated energy -3652.23 a.u., as depicted in Fig. S10c.

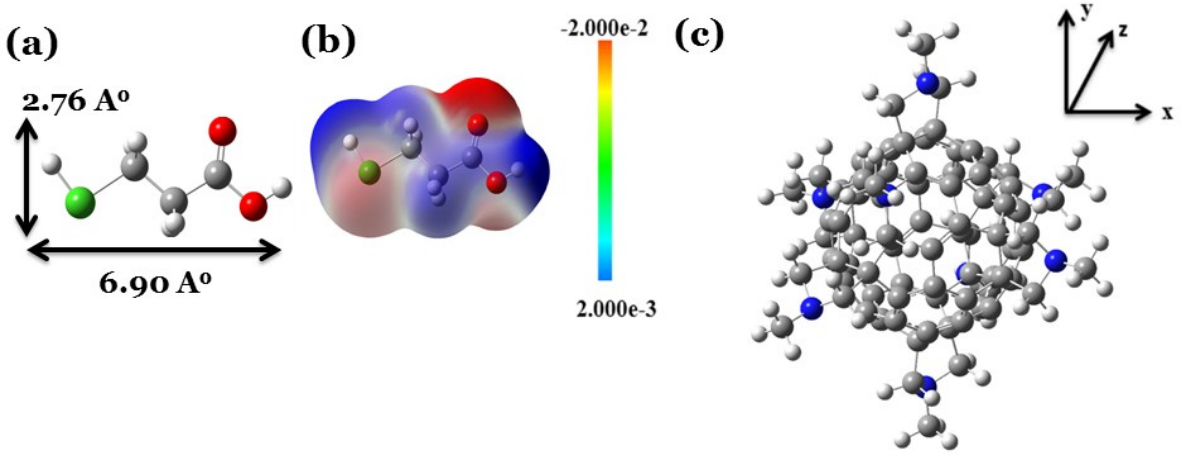

Fig. S10 DFT optimized geometry of 3-MPA (a) and its ESP map (b). (c) Optimized geometry of 8-NMFP.

Spectral overlap of acceptor absorption with donor emission:

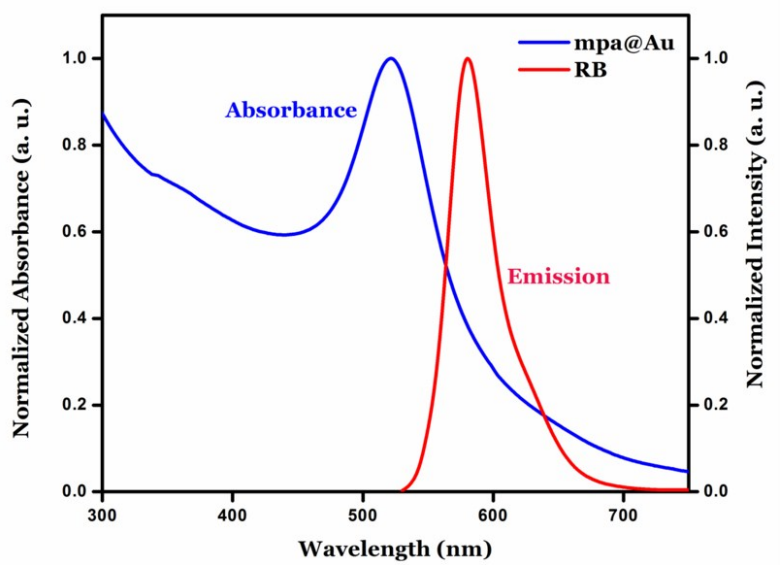

Fig. S11 Spectral overlap of 8-NMFP- mpa@Au absorption spectrum with emission of pure dye RB spectrum.

References:

1. S. Leach, M. Vervloet, A. Desprès, E. Bréheret, J. P. Hare, T. John Dennis, H. W. Kroto, R. Taylor and D. R. M. Walton, *Chem. Phys.*, 1992, **160**, 451-466.
2. S. J. Cyvin, E. Brendsdal, B. N. Cyvin and J. Brunvoll, *Chem. Phys. Lett.*, 1988, **143**, 377-380.
3. W. Haiss, N. T. K. Thanh, J. Aveyard and D. G. Fernig, *Anal. Chem.*, 2007, **79**, 4215-4221.