Aggregation-induced enhanced green light emission from a simple donor-π-acceptor (D-π-A) material: A structure-property relationship study

Vinod Kumar Gupta and Ram Adhar Singh*

Department of Chemistry, Centre of Advanced Study, Institute of Science, Banaras Hindu University, Varanasi-221 005, INDIA

Email: **prrasingh@gmail.com**

Supporting Information

NMR

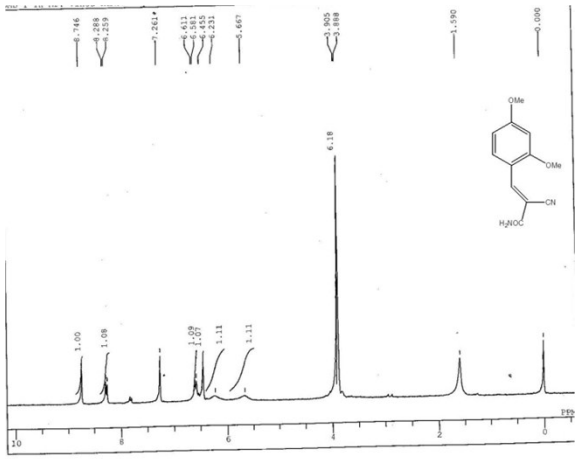

Fig. S1 ^{1}H NMR spectrum of A1.

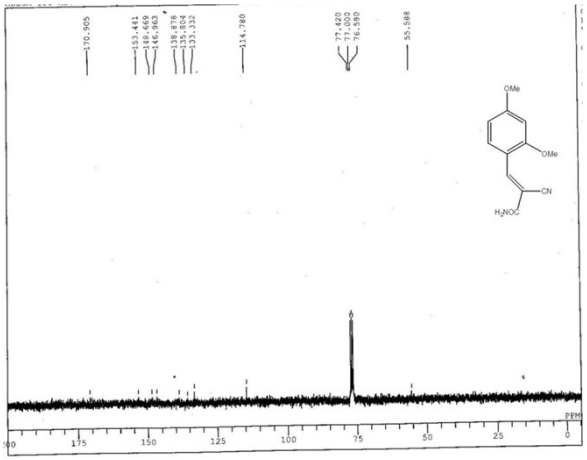

Fig. S2 ^{13}C NMR spectrum of A1.

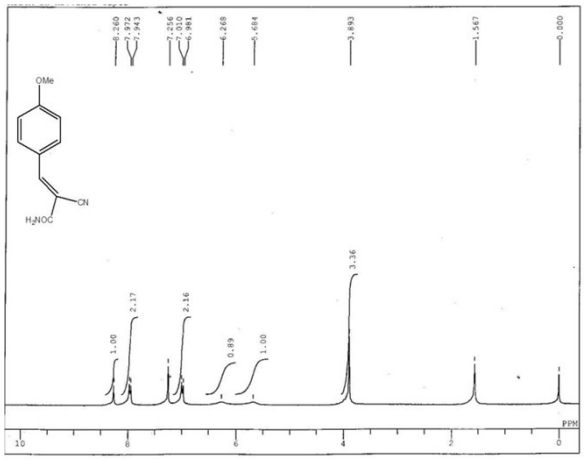

Fig. S3 ^{1}H NMR spectrum of A2.

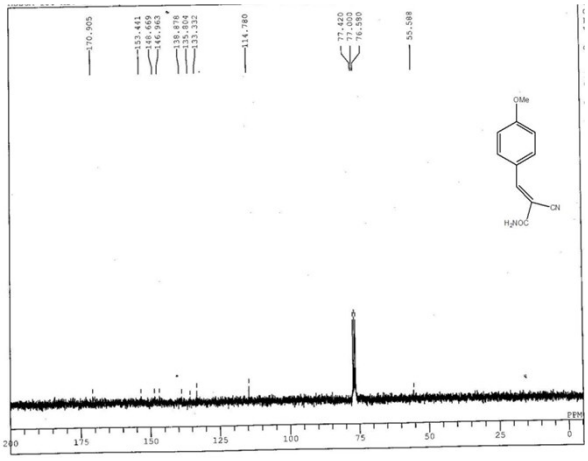

Fig. S4 ^{13}C NMR spectrum of A2.

FT-IR

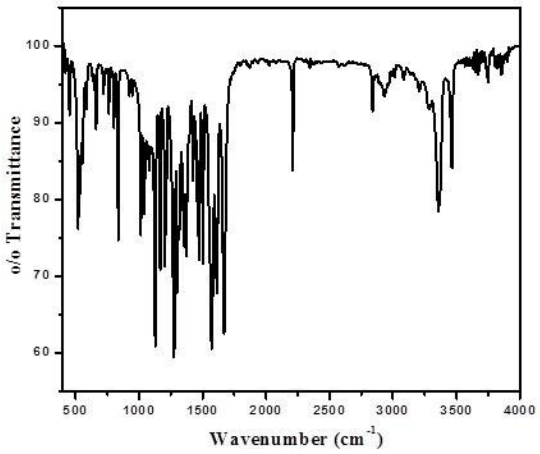

Fig. S5 FT-IR spectrum of A1.

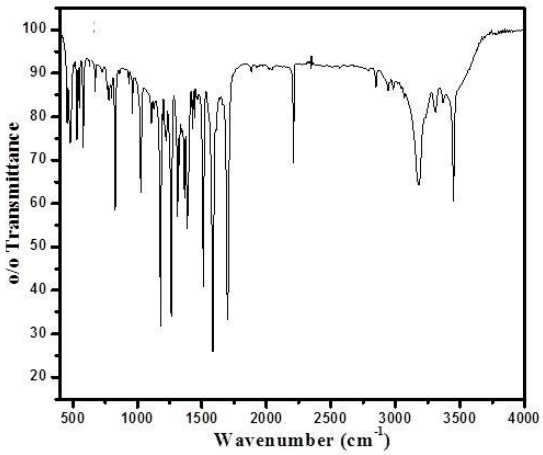

Fig. S6 FT-IR spectrum of A2.

Single crystal growth and crystallographic data

The single crystals of A1 and A2 were grown from the saturated 1:1 acetone–methanol and 1:1 acetone–acetonitrile solution by slow evaporation technique, respectively. For this purpose, saturated solutions of compounds were kept at room temperature for slow evaporation of solvent. After a couple of days, small crystals were harvested and used for X-ray analysis.

Table S1 Structural parameters for A1 and A2

	A1	**A2**
Empirical formula	C_{12} H_{12} N_2 O_3	C_{11} H_{10} N_2 O_2
M_r	232.24	202.21
Crystal size (mm)	0.4×0.2×0.1	0.4×0.3×0.2
Crystal system	monoclinic	monoclinic
Space group	P 2_1/n	P 2_1/c
a [Å]	10.5310(11)	3.9225(3)
b [Å]	15.6321(15)	10.7762(9)
c [Å]	13.7351(18)	23.142(2)
α [°]	90.00	90.00
β [°]	94.071(10)	93.453(7)
γ [°]	90.00	90.00
V [Å^3]	2255.4(4)	976.43(14)
Z	8	4
D [g cm^{-3}]	1.368	1.376
T [K]	293(2)	293(2)
λ [Å]	0.71073	0.71073
μ [mm^{-1}]	0.100	0.097
F(000)	854	424
h	-8 to 13	-4 to 3
k	-21 to 16	-12 to 14
l	-18 to 17	-29 to 30
θ range for data collection (°)	3.00 to 29.25	3.25 to 29.08
Reflections measured	10852	3726
Reflections unique	5167	2119
Data with $F_o > 2\sigma(F_o)$	2669	1414
Parameters refined	311	138
final R indices	0.0818	0.0466
final wR indices	0.2164	0.1021
goodness of fit	0.981	1.036
ccdc number	**1486589**	**1486590**

Table S2 Bond Lengths (Å) and Bond Angles (deg) in the Structures Studied.

		A1			
O(2)–C(2)	1.363(4)	O(2)–C(12)	1.428(4)	O(1)–C(4)	1.360(4)
O(1)–C(11)	1.431(6)	N(2)–C(10)	1.326(5)	N(1)–C(9)	1.153(4)
O(3)–C(10)	1.239(5)	C(9)–C(8)	1.413(4)	C(8)–C(7)	1.350(4)
C(8)–C(10)	1.494(6)	C(7)–C(1)	1.433(4)		
C(2)–O(2)–C12	118.2(3)	C(4)–O(1)–C(11)	118.1(3)	N(1)–C(9)–C(8)	177.6(4)
C(9)–C(8)–C(7)	123.5(3)	C(9)–C(8)–C(10)	117.5(3)	C(7)–C(8)–C(10)	119.0(3)
C(8)–C(7)–C(1)	132.8(3)	O(2)–C(2)–C1	116.5(3)	O(2)–C(2)–C(3)	122.7(3)
C(7)–C(1)–C(6)	124.6(3)	O(1)–C(4)–C(5)	124.1(3)	O(1)–C(4)–C(3)	114.5(3)
N(2)–C(10)–O(3)	121.7(4)	N(2)–C(10)–C(8)	117.5(3)	O(3)–C(10)–C(8)	120.8(4)
		A2			
O(2)–C(10)	1.231(2)	O(1)–C(4)	1.365(2)	O(1)–C(11)	1.422(2)
C(7)–C(8)	1.342(2)	C(7)–C(1)	1.445(2)	C(8)–C(10)	1.501(2)
C(8)–C(9)	1.427(2)	N(2)–C(10)	1.322(2)	N(1)–C(9)	1.146(3)
C(4)–O(1)–C(11)	118.3(1)	C(8)–C(7)–C(1)	133.5(2)	C(7)–C(8)–C(10)	117.9(1)
C(7)–C(8)–C(9)	124.4(2)	C(10)–C(8)–C(9)	117.7(1)	C(7)–C(1)–C(6)	126.3(2)
C(7)–C(1)–C(2)	116.9(1)	O(1)–C(4)–C(3)	115.4(1)	O(1)–C(4)–C(5)	124.6(1)
O(2)–C(10)–C(8)	119.9(2)	O(2)–C(10)–N(2)	122.4(2)	C(8)–C(10)–N(2)	117.7(2)
C(8)–C(9)–N(1)	177.5(2)				

Absorption and fluorescence spectra

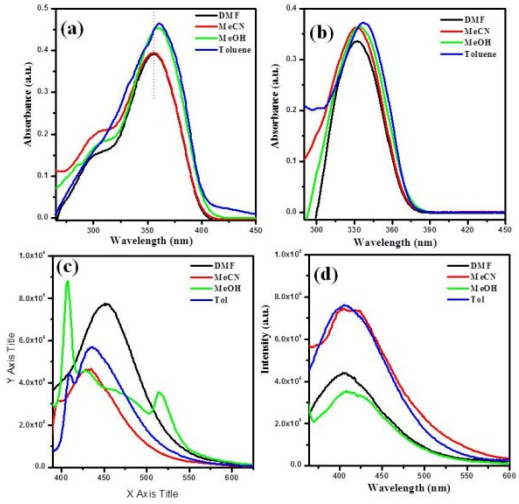

Fig. S7 (a) Absorption spectra of A1, (b) absorption spectra of A2, (c) fluorescence spectra of A1 and (d) fluorescence spectra of A2 in different solvents with molar concentration 1.0×10^{-5} M.

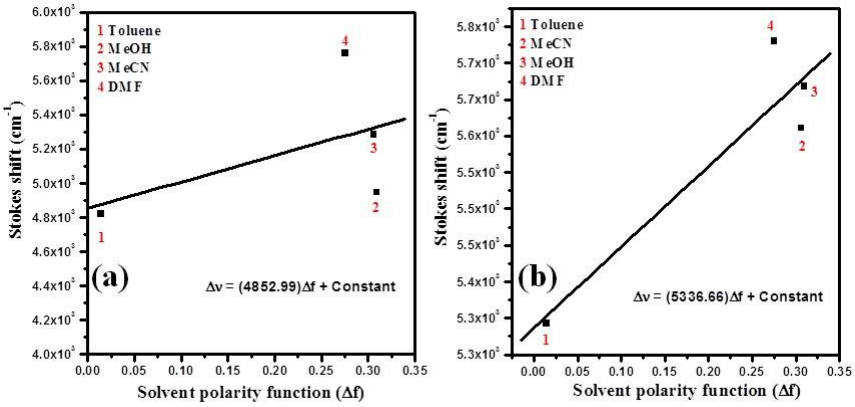

Fig. S8 Lippert-Mataga plots for (a) A1 and (b) A2.

Quantum yield

The relative fluorescence quantum yield (Φ_f) of compounds were calculated in different organic solvents using widely spread method introduced by Parker and Rees (equation 1),[1]

$$\Phi_f^i = \Phi_f^s \frac{f_s(\lambda_{ex})}{f_i(\lambda_{ex})} \frac{\int_{\lambda_{em}} F^i(\lambda_{em})}{\int_{\lambda_{em}} F^s(\lambda_{em})} \frac{n_i^2}{n_s^2} \quad (1)$$

where i stands for the sample and s for standard; n is the refractive index of the solvent used, term $\int_{\lambda em}$ F (λ_{em}) represents the area under the fluorescence curve and f_s (λ_{ex}) = $1\text{-}10^{-Ax\ (\lambda ex)}$; where A_x is the absorbance. Anthracene has been used as a reference material for the calculation of relative quantum yield.

Differential thermal analysis (DTA) and activation energy calculation

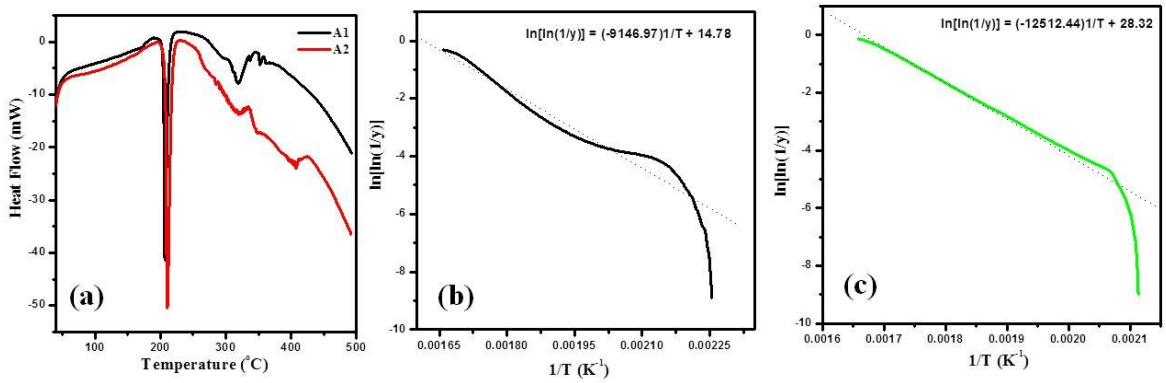

Fig. S9 (a) DTA curve of compounds A1 and A2, (b) Thermal activation energy plot of A1 and (c) Thermal activation energy plot of A2.

The energy of activation (E_a) associated with each stage of decomposition is given by the equation:[2]

$$\ln\left[\ln\left(\frac{1}{y}\right)\right] = \left(-\frac{E_a}{R}\right)\frac{1}{T} + Constant \qquad (2)$$

Where $y = (W_t - W_\infty)/(W_o - W_\infty)$ is the fraction of the number of initial molecules not yet decomposed, R is the gas constant, T is the absolute temperature, W_t is the weight at any time t, W_∞ is the weight at infinite time. The energy of activation may be computed from the slope of the ln[ln(1/y)] vs. 1/T plot which results a straight line. The plot is given in Fig. S 9b and 9c.

References

1 K. Rurack and M. Spieles, Fluorescence quantum yields of a series of red and near-infrared dyes emitting at 600-1000 nm, *Anal. Chem.*, 2011, **83**, 1232–1242.

2 A. Broido, A simple, sensitive graphical method of treating thermogravimetric analysis data, *J. Polymer Sci.*, 1969, 7, 1761–1773.