Photochemical &
Photobiological
Sciences

ROYAL SOCIETY
OF CHEMISTRY

www.rsc.org/pps

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Quinone-Bodipy H-bonding interaction over π-stacking in toluene

Animesh Karmakar[a], Soumyaditya Mula[b], Kalyan Ghosh[c], Tandrima Chaudhuri[a]*, Neelam Shivran[b], Manas Banerjee[c] and Subrata Chattopadhyay[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Quinone type compounds (*o*-chloranil, *p*-chloranil and DDQ) demonstrate excellent H-bonding interaction with a *meso*-phenol Bodipy dye (**1**) both in the ground and excited state in non-polar toluene medium. Spectroscopic detection of isosbestic absorption occurs with both quinones and fullerenes but only quinones form isoemissive complexes with the dye **1**. ^{1}H NMR study and Monte Carlo global minima searching justified the above fact with efficiency.

Introduction

Weak interaction prevails in molecular assemblies are recently widely studied because of its vast application[1]. Much effort has been devoted during the past two decades in trying to understand the pivotal forces of non-covalent interactions in molecular assemblies. Generally the operational nonbonding interacting forces for the generation of host-guest assemblies are π-π interaction[2], hydrogen bonding[3], hydrophobic[4] and van der Waals[5] interactions. Change(s) in any or a combination of these interactions may lead to different orientation of the host and the guest in the assembly with respect to each other.

Bodipy class of compounds is getting immense attention from every field of science in recent years due to their tunable fluorescene properties.[6] Few reports are available on supramolecular aggregation of Bodipy compounds based on π-π interaction and hydrogen bonding.[7]

We investigate photophysically the the variety of association of five different well known electron acceptors i.e. two fullerenes- C_{70} (**A1**) and C_{60} (**A2**), and three differently substituted quinone type compounds- *o*-chloranil (**A3**), *p*-chloranil (**A4**) and dichloro-dicyano quinine (DDQ) (**A5**) with a meso-phenol BODIPY dye 2,6-Diethyl-4,4-difluoro- 1,3,5,7-tetramethyl-8-(4’-hydroxyphenyl)-4-bora-3a,4a-diaza-s-indecene (**1**) (Fig. 1) in both ground and excited states. Here photophysics can differentiate fullerenes from quinone type compounds. Thus quinone type commpounds can be recognized photophysically by this BODIPY dye (**1**) as no iso-emissive is formed with fullerenes in toluene. However, ^{1}H NMR study and Monte Carlo simulation further distinguished this interaction on the basis of predominance of H-bonding interaction over π-stacking in case of quinone type compounds. To the best of our knowledge, this is the first report of H-bonding interaction in a Bodipy-Quinone system.

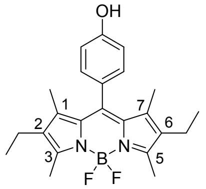


Figure 1 Chemical structure of *meso*-phenol Bodipy dye **1**.

Experimental

Materials and Methods

Toluene used as solvent was of HPLC grade. Two fullerenes C_{70} (**A1**) and C_{60} (**A2**) and three differently substituted quinone type compounds i.e. *o*-chloranil, *p*-chloranil, Dichloro-dicyano quinone (DDQ) (**A3** – **A5**) used as well known electron acceptors were purchased from Aldrich. The concentration of acceptors were taken in the range (10^{-4} – 10^{-5}) M in all the spectral measurements. The concentration of dye **1** was of the order of (10^{-5} – 10^{-6}) M.

Instruments used

The absorption (UV-Vis) spectral measurements were performed with a Shimadzu UV 1800 spectrophotometer fitted with an electronic temperature controller unit (TCC –240 A). The steady state fluorescence emission and excitation spectra were recorded with a Hitachi F-4500 spectrofluorometer equipped with a temperature controlled cell holder. Temperature was controlled within ± 0.1 K by circulating water from a constant temperature bath (Heto Holten, Denmark). ^{1}H NMR spectra were recorded on Bruker 500 spectrometer at 298 K in d_8-toluene. Temperature dependent measurements were carried out in d_8-toluene in the range 298-333 K.

Monte Carlo simulations

Simulation were performed using Spartan’14 molecular modelling software from Wavefuntion Inc. (Irvine, CA, USA). Using Monte Carlo simulation[3a], global minima search for all the five optimized complexes neglecting solvent were performed using Merck molecular force-field calculations (MMFF).

Synthesis of BODIPY

General procedure for the preparation of **2,6-Diethyl-4,4-difluoro-1,3,5,7-tetramethyl-8-(4'-hydroxyphenyl)-4-bora-3a,4a-diaza-s-indecene (1)**. A mixture of kryptopyrrole (0.500 g, 4.07 mmol), *p*-hydroxybenzaldehyde (0.226 g, 1.85 mmol) and *p*-toluenesulphonic acid (0.015 g) in dry THF (70 mL) was stirred at room temperature for 24 h. DDQ (0.420 g, 1.85 mmol) was added to the resulting deep red solution and stirring continued for 4 h. The mixture was treated with triethylamine (1.56 mL, 11.09 mmol), and stirred for another 1 h. Finally, $BF_3.Et_2O$ (1.39 mL, 11.09 mmol) was added to the mixture in portions during 4 h, and the solution stirred at room temperature overnight. The resulting dark mixture was washed with aqueous saturated $NaHCO_3$, water, and brine and dried. Removal of solvent in vacuo followed by column chromatography of the residue (silica gel, hexane-EtOAc) furnished **1** (0.350 g, 23.4%), which was recrystallized from acetone/cyclohexane to afford red-orange square crystals. Mp: 228 °C; ^{1}H NMR (700 MHz, $(CD_3)_2CO$): δ 0.98 (t, *J* = 7.7 Hz, 6H), 1.41 (s, 6H), 2.34 (q, *J* = 7.7 Hz, 4H), 2.48 (s, 6H), 7.04 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 8.71 (s, 1H); ^{13}C NMR (175 MHz, $(CD_3)_2CO$): δ 10.2, 10.6, 13.0, 15.6, 115.0, 125.4, 128.5, 130.1, 131.5, 137.3, 140.3, 152.0, 157.1; EI-MS (m/z): 396.1 $[M]^+$, 395.4 $[M-1]^+$. Anal. Calcd. For $C_{23}H_{27}BF_2N_2O$: C, 69.71; H, 6.87; N, 7.07%. Found: C, 69.42; H, 6.74; N, 7.22%.

Results and discussions

Photophysical Studies

In the photophysical investigation, both fullerenes (**A1** and **A2**) and quinones (**A3** – **A5**) formed well established absorption isosbestic on titrating with **1** in toluene (Table 1). Along with the change in absorbance, absorption maxima of most of the **A** compounds were shifted to longer wavelengths and were shown in Fig. 2. With the decrease of the absorbance of **A4** (at 285 nm), absorption maxima of dye (**1**) (at 367.5 nm) increases monotonously on titrating with **1** (shown in Fig. 2b inset), giving rise to a set of isosbestic at the juncture and was shown in Fig.2b. Thus all the five acceptors form stable equilibrium with the Bodipy dye (**1**) in toluene medium in the ground state.

Table 1. Isosbestic points appeared on interaction of five acceptors (**A**) with dye **1** in toluene.

System	Absorption isosbestic point at wavelength (nm)	Iso-emissive point at wavelength (nm)
A1/1	490, 544	-
A2/1	389.5, 555.0	-
A3/1	335.5, 419, 438.5	339.6, 424.4
A4/1	325.5	375.8
A5/1	328.5	359, 496

Till date excited state quinone-Bodipy association was not so well established. On titrating the acceptors (**A**) with the dye separately not only fluorescence intensity of **A3**, **A4** and **A5** were quenched but also gave rise to set of iso-emissive points with dye **1** (Fig. 3a). But **A1** and **A2** did not form any iso-emissive with **1** (Fig. 3b). We have to mention here that this excited state equilibrium were as well defined as that of ground state in case of quinone type compounds, but this equilibrium did not at all established with fullerenes (**A1** and **A2**) in the excited state (Table 1).

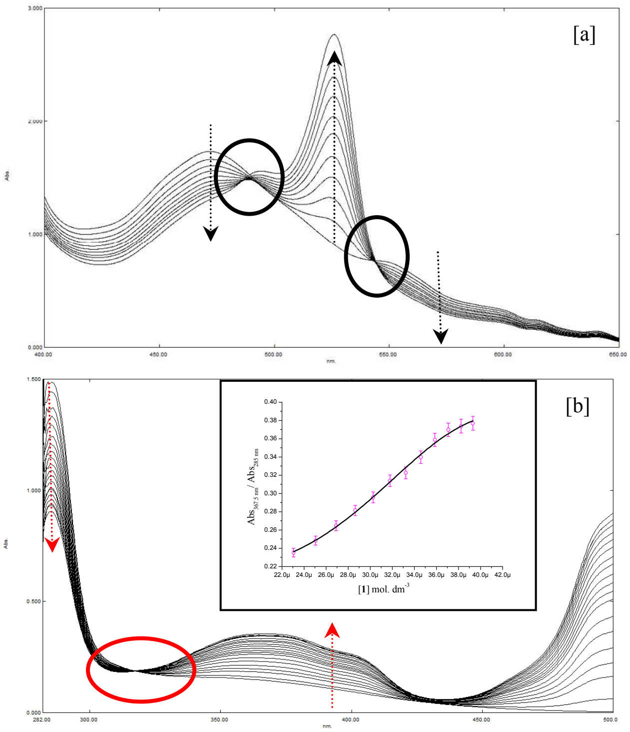
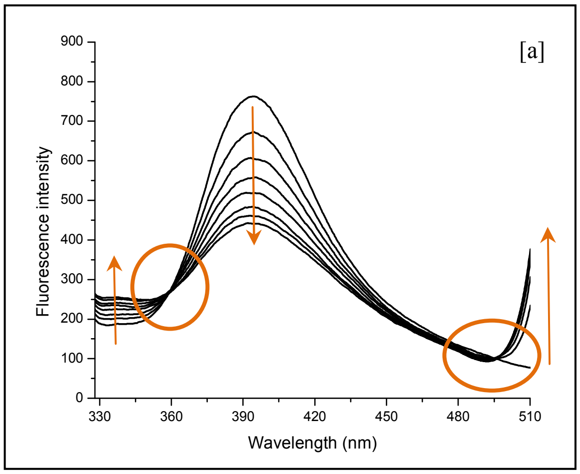


Figure 2. Absorption isosbestic of the electron acceptors by dye **1** in toluene. Concentration of dye **1**: 0.00, 3.843× 10^{-6} , 7.336×10^{-6}, 1.053 ×10^{-5}, 1.345×10^{-5}, 1.614 ×10^{-5}, 1.862×10^{-5}, 2.092×10^{-5} and 2.306×10^{-5} mol dm^{-3} [a] at a fixed concentration (1.027×10^{-4} mol dm^{-3}) of the **A1** solution in toluene [b] At a fixed concentration (1.00×10^{-4} mol dm^{-3}) of the **A4** solution in toluene.



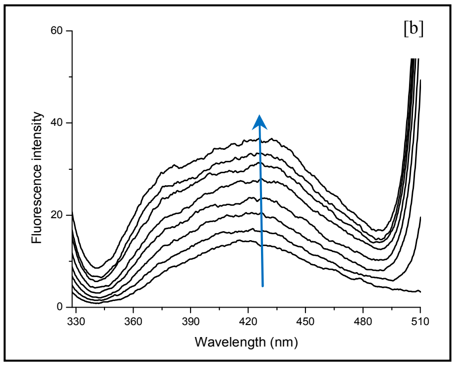
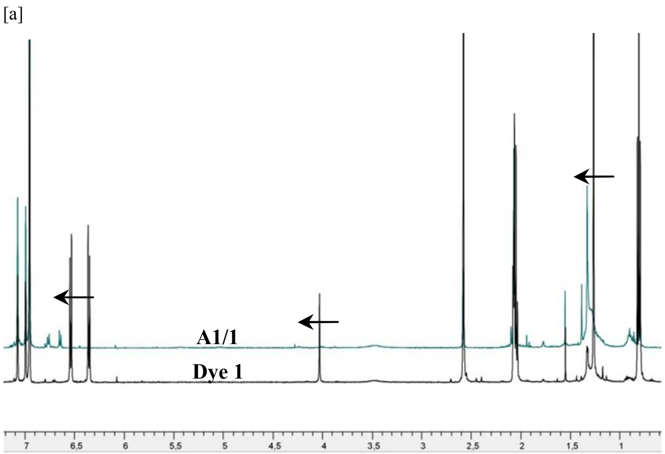


Figure 3. Excited state titration of the electron acceptors by dye **1** in toluene. Concentration of dye **1**: 0.00, 7.336×10^{-6}, 1.345×10^{-5}, 1.862×10^{-5}, 2.306×10^{-5}, 2.69×10^{-5}, 3.026×10^{-5}, 3.323×10^{-5} and 3.587×10^{-5} mol dm^{-3} [a] at a fixed concentration (1.00×10^{-4} mol dm^{-3}) of the **A5** solution in Toluene. [b] At a fixed concentration (1.00×10^{-4} mol dm^{-3}) of the **A2** solution in Toluene. λ_{ex} = 300 nm.

^{1}H NMR Study

Further, to investigate the interaction of the dye **1** with different type of acceptors, we carried out the one-dimentional NMR studies of **A1/1**, **A3/1** and **A5/1** adducts (1:1) in d_8-toluene. The ^{1}H NMR spectrum of **1** showed clean and well separated peaks for different protons (Fig. 4a and S1a). The C8-phenyl protons of the dye **1** appeared as two doublets at δ 6.55 and δ 6.37 ppm, and the phenolic–OH proton signal appeared at δ 4.03 as a singlet. The C1 and C7-methyl protons are shielded by the phenyl ring current and resonate at δ 1.27 ppm, while the C3 and C5-methyl protons resonate at δ 2.58 ppm. For C2 and C6-ethyl groups, the methylene protons signal merged with the d_8-toluene signal at δ 2.04-2.08 ppm and the triplet due to the methyl protons was observed at δ 0.81 ppm.

In the ^{1}H NMR spectra of **A1/1**, the phenyl, phenolic –OH and, the C1 and C7-methyl protons shifted downfield keeping other parts similar (Fig. 4a and S1b). Also the downfield shift of phenyl (155 and 115 Hz) and phenolic –OH protons (125 Hz) are much more than that of C1 and C7-methyl protons (30 Hz). These suggest π-π interaction of **A1** and **1**, and the upper part of the dye (phenyl ring) is nearer to the C_{70} unit.



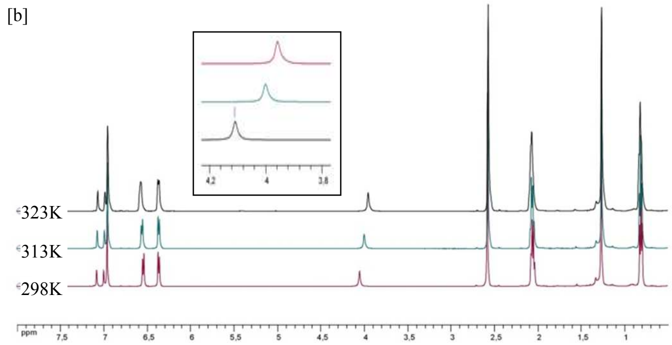


Figure 4. ^{1}H NMR spectra of [a] Dye **1**, merged with **A1/1** (1:1) mixture in d_8-toluene, of [b] **A3/1** (1:1) mixture in d_8-toluene at 298K, 313K and at 323K.

Alternatively, in the ^{1}H NMR spectra of **A3/1**(Fig. 4b and S1c) and **A5/1** (Fig. S1d) complexes, all the methyl, methelene and phenyl protons signals of **1** appeared at the similar positions as that of **1** but the –OH proton singlets were shifted downfield by 40.0 and 35.0 Hz respectively. This is a clear indication of intermolecular H-bonding interaction of the phenolic –OH proton with the carbonyl group of **A3** and **A5** and the interaction with the **A3** is stronger than that of with **A5**. With increase in temperature of **A3/1c** complex in d_8-toluene from 298 to 323 K, it was observed that the phenolic –OH proton signal shifted to higher fields, it experienced shielding effect of up to 73.5 Hz keeping all other methyl, methelene and phenyl protons signals similar (Fig. 4b S2a and S2b). All these confirm the intermolecular H-bonding interaction of the phenolic –OH proton with **A3** moiety.[8]

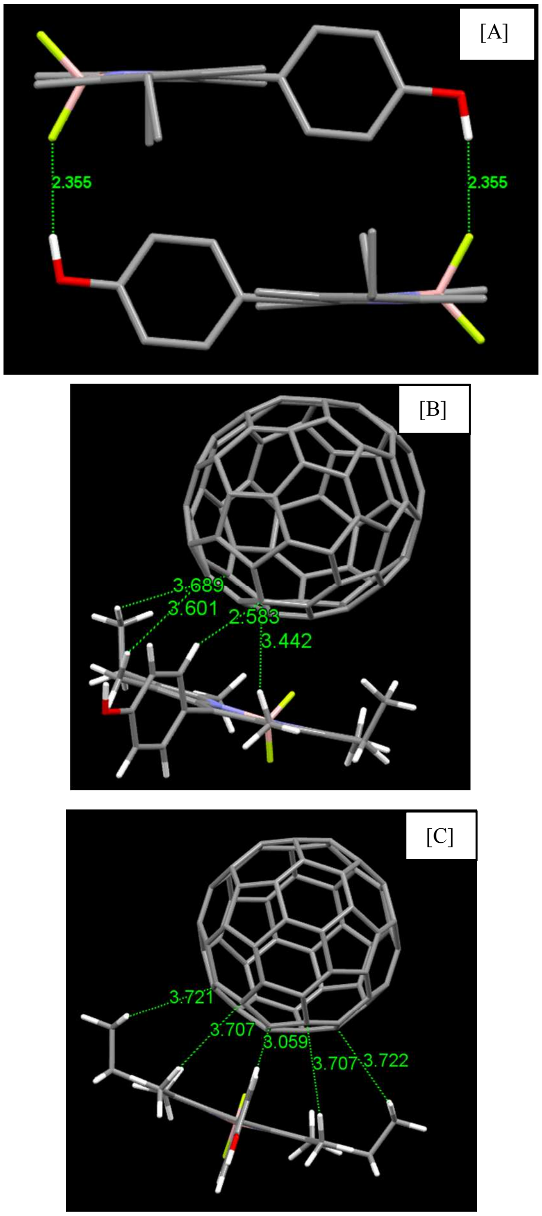
Monte Carlo Simulation

A rigorous Monte Carlo (MC) conformational search protocol[9] was employed for better understanding of these associated complexes. Till date weak intermolecular interactions (H-bonding, CT, vdW and hydrophobic) are mostly studied using density based geometry optimization calculation of the adduct structures.[10] It is well known that all optimization methods employing quantum and semi classical calculations find local minima or transition structures, near to the starting structure. Again DFT based calculation has the disadvantage related to the best choice of functional for the system of interest. Many DFT methods perform poorly for hydrogen-bonded systems and other weakly-bound intermolecular complexes.[11] However, conformational searching demands searches for the global minimum among numerous local minima and energy barriers. Thus conformational global searching of the H-bonded adducts were accomplished by means of Monte Carlo protocol[12a] based on force-field molecular mechanics[12b] available in Spartan 14 suite of programs. Search over about 64 conformers gives the minimum energy structure shown in Fig. 5. MC method is preferred over rigorous quantum mechanical methods (abinitio/DFT) due to the flexible, low minimum (energy) structures of the present systems.

Fig. 5 gives the MC simulated global minimum conformers of the five complexes. The dye 1 itself exists as weak H-bonded dimer having H-bond distance 2.35Å, as it contains electronegative –F (in –BF_2 unit) as well as phenolic –OH group. Fig. 5A is the global minimum conformer out of total 64 possible conformers of **1** dimer in gas phase. The effect of solvation on the tuning of dimer interaction is neglected on consideration of cancellation of similar magnitudes of small energy in the process of dimerisation.

Table 2. Parameters of Monte Carlo global minimum conformers.

System	Distances (Å), Angle between Bodipy chromophore and aromatic ring of acceptor (°)		Dipolemoment (D)	Number of Conformers possible
	$C_g - C_g$ distance (Å), Angle (i,j)	H-bond (Å)		
A1/1	4.32, 7.45	-	23.69	8
A2/1	4.66, 5.38	-	20.07	8
A3/1	4.06, 4.00	1.741	2.15	64
A4/1	3.95, 2.87	1.731	0.89	64
A5/1	3.89, 3.69	1.745	0.43	64



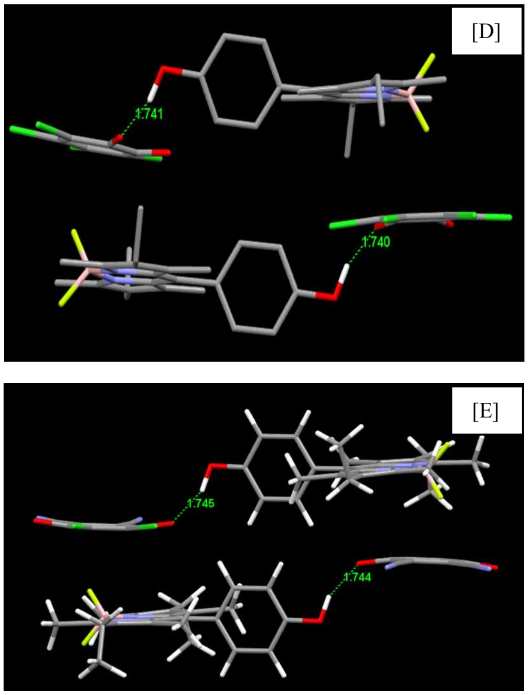


Figure 5. Wireframe structure of Monte Carlo global minimum conformers of [A] **1** exists as H-bonded dimer, [B] **A1/1** adduct, [C] **A2/1** adduct, [D] **A3/1** adduct, [E] **A4/1** adduct and [F] **A5/1** adduct in gas phase. All hydrogen except -OH protons those involved in hydrogen bonding have been removed for clarity in the first and fourth perspectives.

Only 8 confomers are possible for fullerene-dye (**A1/1** or **A2/1**) adducts. Fullerenes experienced strong π-π interaction with **1**, as Fig. 5B and 5C show that the upper part of the dye where the density of π-cloud is maximum[13], is nearer to fullerenes. This is supporting the observation in NMR study. On the other hand, the clear evidence of H-bonding in quinone-Bodipy (2:2) association was observed in Fig. 5(D–F) along with the π-π interaction. However in case of fullerenes only π-π interaction is feasible with the Bodipy dye. The parameters of H-bonding and π-stacking interaction i.e. H-O distances and angle between the aromatic rings and centre of gravity (C_g) distances respectively were shown in Table 2. On the basis of π-cloud C_g distances, of dye **1** chromophore and 6:6 fused rings of fullerenes lying above the dye, C_{70} forms the most stable complex with the dye. In case of quinone type compounds possibly both H-bonding and π-π interactions were taking place. The angle between the Bodipy chromophore and the aromatic rings and the π-cloud centre of gravity (C_g) distances for all the five interacting system were shown in Table 2. This table indicate that **A3** (*o*-chloranil) had least and **A5** (DDQ) had most contribution among the three quinone type compounds (**A3** – **A5**) for π- π interaction with **1** dye. And *p*-chloranil had shortest H-bond distance among the three. However ^{1}H NMR study indicates that **A3** shows larger shift of phenolic proton on interacting with **1** in toluene medium. Thus considering combination of both H-bonding and π-stacking, **A3** (*o*-chloranil) demonstrated highest binding adduct with the dye.

Conclusions

In summary *meso*-phenol Bodipy (**1**) chromophore is a very suitable system for evaluating a taxing Monte Carlo calculation in the presence of fullerenes like π-stacking or quinone like π-stacked H-bonded adducts. It is because of the ^{1}H NMR study and Monte Carlo simulation incorporating fullerenes or quinone like adducts of **1** that the missing of iso-emissive for the fullerene-dye adducts can be explained neatly and precisely. Further extension of the work in this context is being carried out in our laboratory.

Acknowledgements

Author (TC) acknowledges the grant received from UGC funded Major project, F.42-390/2013(SR)/dated 25/03/2013.

Notes and references

[a]Department of Chemistry, Dr. Bhupendranath Dutta Smriti Mahavidyalaya, Burdwan-713407, India.
tanchem_bu@yahoo.co.in
[b]Bio-Organic Division, Bhabha Atomic Research Centre, Trombay, Mumbai-400085, India.
[c]Department of Chemistry,The University of Burdwan, Golapbag, Burdwan-713104, India.

Electronic Supplementary Information (ESI) available: [copies of NMR spectra, isosbestic and iso-emissive spectra of all five systems and MC conformers coordinates are given]. See DOI: 10.1039/c000000x/

1 (a) M. Olofsson, S. Kalinin, J. Zdunek, M. Oliveberg, L. B.-A, Johansson, Tryptophan–BODIPY: A versatile donor–acceptor pair for probing generic changes of intraprotein distances, *J. Phys. Chem. Chem. Phys*., 2006, **8**, 3130; (b) W. Zhu, W. Li, C. Wang, J. Cui, H. Yang, Y. Jiang and G. Li, CB[8]-based rotaxane as a useful platform for sensitive detection and discrimination of explosives, *J. Chem. Sci*., 2013, **4**, 3583; (c) A. Coskun, J. M. Spruell, G. Barin, W. R. Dichtel, A. H. Flood, Y. Y. Botros and J. Fraser Stoddart, High hopes: can molecular electronics realise its potential? *J. Chem. Soc. Rev.,* 2012, **41**, 4827**.**

2 (a) S. J. Cantrill, A. R. Pease and J. F. Stoddart, A molecular meccano kit, *J. Chem. Soc., Dalton Trans*., 2000, 3715; (b) J. Rebek and D. Nemeth, Molecular recognition: ionic and aromatic stacking interactions bind complementary functional groups in a molecular cleft, *J. Am. Chem. Soc*., 1986, **108**, 5637; (c) S. K. Burley and G. A. Petsko, Dimerization energetics of benzene and aromatic amino acid side chains, *J. Am. Chem. Soc*., 1986, **108**, 7995; (d) A. D. Hamilton and D. V. Engen, . Induced fit in synthetic receptors: nucleotide base recognition by a molecular hinge, *J. Am. Chem. Soc*., 1987, **109**, 5035; (e) S. C. Zimmerman and C. M. Vanzyl, Rigid molecular tweezers: synthesis, characterization, and complexation chemistry of a diacridine, *J. Am. Chem. Soc*., 1987, **109**, 7894; (f) J. C. Nelson, J. G. Saven, J. S. Moore and P. G. Wolynes, Solvophobically Driven Folding of Nonbiological Oligomers,*Science*, 1997, **277**, 1793; (g) C. A. Hunter, Arene—Arene Interactions: Electrostatic or Charge Transfer? *Angew. Chem., Int. Ed. Engl*., 1993, **32**, 1584; (h) C. A. Hunter, Meldola Lecture. The role of aromatic interactions in molecular recognition, *Chem. Soc. Rev*., 1994, **23**, 101; (i) S. B. Ferguson and F. Diederich, Electron Donor-Acceptor Interactions in Host-Guest Complexes in Organic Solutions, *Angew. Chem., Int. Ed. Engl*., 1986, **25**, 1127; (j) M. Nishio and M. Hirota, CH/π interaction: Implications in organic chemistry, *Tetrahedron*, 1989, **45**, 7201.

3 (a) S. Ghosh, T. Chaudhuri and C. Mukhopadhyay, The new threading system 2-benzyl-5,6-dimethyl-1H-benzo[d]imidazolium – dibenzo-24-crown-8: a model for Monte Carlo calculations incorporating an anion for the first time in threaded structures, *RSC Adv.* 2014, **4**, 18835; (b) S. Ghosh, T. Chaudhuri, A. M. Schmiedekamp, E. Padmanaban and C. Mukhopadhyay, A 2,2′-bis(benzimidazolium)-dibenzo[24]crown[8] rigid pseudorotaxane system, *Tetrahedron*, 2014, **70**, 6885. (c) M. Kotera, J. M. Lehn and J. P. Vigneron,Self-assembled supramolecular rigid rods, *J. Chem. Soc., Chem. Commun*., 1994, 197; (d) R. P. Sijbesma and E. W. Meijer, Self-assembly of well-defined structures by hydrogen bonding, *Curr. Opin. Colloid Interface Sci.*, 1999, **4**, 24; (e) G. A. Jeffrey, *An Introduction to Hydrogen Bonding; Oxford University Press: New York*, 1997.

4 (a) A. Ben-Naim, *Hydrophobic Interactions; Plenum Press: New York & London*, 1980; (b) A. C. Bhasikuttan, J. Mohanty, W. M. Nau and H. Pal, Efficient fluorescence enhancement and cooperative binding of an organic dye in a supra-biomolecular host-protein assembly, *Angew. Chem., Int. Ed. Engl*., 2007, **46**, 4120.

5 (a) A. G. Street and S. L. Mayo, Intrinsic b-sheet propensities result from van der Waals interactions between side chains and the local backbone, *Proc. Natl. Acad. Sci. U.S.A*., 1999, **96**, 9074; (b) K. Ohta, M. Ikejima, M. Moriya, H. Hasebe and I. Yamamoto, Disk-like liquid crystals of transition metal complexes. Part 20.Pursuit of chemistry to directly visualize van der Waals interactions, *J. Mater. Chem*., 1998, **8**, 1971.

6 (a) A. Loudet and K. Burgess, BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties, *Chem. Rev.* 2007, **107**, 4891; (b) N. Boens, V. Leen and W. Dehaen,Fluorescent indicators based on BODIPY, *Chem. Soc. Rev.* 2012, **41**, 1130; (c) A. Kamkaew, S. H. Lim, H. B. Lee, L. V. Kiew, L. Y., BODIPY dyes in photodynamic therapy, *Chem. Soc. Rev.* 2013, **42**, 77; (d) H. Lu, J. Mack, Y. Yanga and Z. Shen, Structural modification strategies for the rational design of red/NIR region BODIPYs, *Chem. Soc. Rev.* 2014, **43**, 4778; (e) A. Bessette and G. S. Hanan, Design, synthesis and photophysical studies of dipyrromethene-based materials: insights into their applications in organic photovoltaic devices, *Chem. Soc. Rev.* 2014, **43**, 3342. (f) S. Mula, A. Roy, M. Banerjee, T. Chaudhuri, K. Dasgupta and S. Chattopadhyay, Design and Development of a New Pyrromethene Dye with Improved Photostability and Lasing Efficiency: Theoretical Rationalization of Photophysical and Photochemical Properties, *J. Org. Chem.* 2008, **73**, 2146;(g) S. Mula, K.

Elliott, A. Harriman and R. Ziessel, Energy Transfer by Way of an Exciplex Intermediate in Flexible Boron Dipyrromethene-Based Allosteric Architectures, *J. Phys. Chem. A*, 2010, **114**, 10515; (h) N. Shivran, S. Mula, T. K. Ghanty and S. Chattopadhyay,Steric Strain Release-Directed Regioselective Functionalization of meso-Methyl Bodipy Dyes, *Org. Lett.* 2011, **13**, 5870. (i) M. Gupta, S. Mula, M. Tyagi, T. K. Ghanty, S. Murudkar, A. K. Ray and S. Chattopadhyay, Rational Design of Boradiazaindacene (BODIPY)-Based Functional Molecules*, Chem.−Eur. J.* 2013, **19**, 17766. (j) K. K. Jagtap, N. Shivran, S. Mula, D. B. Naik, S. K. Sarkar, T. Mukherjee, D. K. Maity and A. K. Ray, Change of Boron Substitution Improves the Lasing Performance of Bodipy Dyes: A Mechanistic Rationalisation,*Chem.−Eur. J.* 2013, **19**, 702.

7 (a) F. Camerel, L. Bonardi, M. Schmutz and R. Ziessel, Highly Luminescent Gels and Mesogens Based on Elaborated Borondipyrromethenes., *J. Am. Chem. Soc.* 2006, **128**, 4548; (b) S. Frein, F. Camerel, R. Ziessel, J. Barberá and R. Deschenaux, Highly Fluorecent Liquid-Crystalline Dendrimers Based on Borondipyrromethene Dyes, *Chem. Mater.* 2009, **121**, 3950.

8 V. Lazić, M. Jurković, T. Jednačak, T. Hrenar, J. P. Vuković, P. Novak, Intra- and intermolecular hydrogen bonding in acetylacetone and benzoylacetone derived enaminone derivatives, *J. Mole. Struc*. 2015, **1079**, 243.

9 (a) G. Chang, W. C. Guida and W. C. Still, An internal-coordinate Monte Carlo method for searching conformational space, *J. Am. Chem. Soc.,* 1989, **111**, 4379; (b) J. Kong, C. A. White, A. I. Krylov, C. D. Sherrill, R. D. Adamson, T. R. Furlani, M. S. Lee, A. M. Lee, S. R. Gwaltney, T. R. Adams, C. Ochsenfeld, A. T. B. Gilbert, G. S. Kedziora, V. A. Rassolov, D. R. Maurice, N. Nair, Y. Shao, N. A. Besley, P. E. Maslen, J. P. Dombroski, H. Daschel, W. Zhang, P. P. Korambath, J. Baker, E. F. C. Byrd, T. V. Voorhis, M. Oumi, S. Hirata, C. P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B. G. Johnson, P. M. W. Gill, M. Head-Gordon and J. A. Pople, Q-Chem 2.0: a high-performance *ab initio* electronic structure program package, *J. Comput. Chem*., 2000, **21**, 1532.

10 (a) S. J. Cantrill, A. R. Pease and J. F. Stoddart, *J. Chem. Soc., Dalton Trans*., 2000, 3715; (b) A. C. Bhasikuttan, J. Mohanty, W. M. Nau and H. Pal, *Angew. Chem., Int. Ed. Engl.*, 2007, **46**, 4120; (c) R. Baer, E. Livshits and U. Salzner, *Annual Review of Physical Chemistry*, 2010, **61,** 85; (d) S. S. Velu, F. Di Meo, P. Trouillas, J-C. S.-G. and J.-F, F. Weber, *J. Nat. Prod.,* 2013, 76, 538.

11 D. S. Sholl, J. A. Steckel, Density Function Theory A Practical Introduction, *John Wiley & Sons*. 2009, pp-1, Ch. 9.

12 (a) G. Chang, W.C. Guida, W.C. Still, *J. Am. Chem. Soc.* 111 (1989) 4379.(b) J. Kong, C.A. White, A.I. Krylov, C.D. Sherrill, R.D. Adamson, T.R. Furlani, M.S. Lee, A.M. Lee, S.R. Gwaltney, T.R. Adams, C. Ochsenfeld, A.T.B. Gilbert, G.S. Kedziora, V.A. Rassolov, D.R. Maurice, N. Nair, Y. Shao, N.A. Besley, P.E. Maslen, J.P. Dombroski, H. Daschel,W.Zhang, P.P. Korambath, J. Baker, E.F.C. Byrd, T.VanVoorhis, M. Oumi, S. Hirata, C.P. Hsu, N. Ishikawa, J. Florian, A. Warshel, B.G. Johnson, P.M.W. Gill, M. Head- Gordon, J.A. Pople, *J. Comput. Chem*. 21 (2000) 1532.

13 T. Chaudhuri, S. Mula, S. Chattopadhyay and M. Banerjee, Photophysical properties of the 8-phenyl analogue of PM567: a theoretical rationalization, *Spectrochimica Acta Part A* 2010, **75***,* 739.