DOI: https://doi.org/10.36094/sc.v89.2023.Study_of_Supramolecular_Interaction.Saha.125

ARTICLE

Sci. and Cult. 89 (3–4) : 125-131 (2023)

STUDY OF SUPRAMOLECULAR INTERACTION OF N-METHYL FULLEROPYRROLIDINE WITH FREE-BASE AND ZINC PORPHYRIN IN SOLUTION

SHIV SANKAR SAHA[a], SUBRATA NAYAK[a], SHALMALI BHATTACHARYA[b], SRINJAY BID[c], MOUMITA BOSE[d] AND SUMANTA BHATTACHARYA[a]*

*The present work reports the non-covalent interaction of N-methyl fulleropyrrolidine (**1**) with a designed free-base (2) and zinc porphyrin (3) in solution. Appreciable ground state interaction of 1 with 2 and 3 occurs in 1,2-dichlorobenzene (DCB). Steady state fluorescence experiment elicits significant quenching of the fluorescence of both 2 and 3 in presence of 1 in DCB and this phenomenon is nicely utilized to determine the binding constant of 1-2 and 1-3 systems as 8,740 and 15,590 $dm^3 \times mol^{-1}$, respectively, in DCB. Time resolved fluorescence experiment reveals that deactivation of the photoexcited 2 and 3 in presence of 1 occurs* via *static quenching mechanism. Semiempirical PM3 calculations have generated the optimized geometric structure of 1-2 and 1-3 systems in* vacuo*. Heat of formation values for the said systems, namely, 1-2 and 1-3, evaluated by PM3 calculations corroborate fairly well with the trend in the value of binding constant in DCB.*

Introduction

Both electron transfer (ET) and energy transfer (EnT) phenomena are studied explicitly for artificial molecular and biological systems in recent past[1-5]. Research on design and construction of photovoltaic devices has gained current impetus due to its immense effect for the generation of environmentally friendly photovoltaic systems[6,7]. The idea of research in said area mainly consists of various types of non-covalently and covalently linked systems for the generation of artificial photo induced ET (PET) process[8]. The donor(D)-acceptor(A) pair theory is the main basis behind the design and construction of such systems.

The conjugate system, namely, fullerene-porphyrin, have shown remarkable ability to exhibit both artificial PET and/ PEnT as a result of complementary electronic properties[9,10] and most importantly, formation of self-assembly due to spontaneous interaction between the said components in solution[11-18]. The conjugated π-system of porphyrin macro cycle triggers it to absorb light in the spectral range of visible region and this particular property of porphyrin is judiciously utilized for the preparation and characterization of light-harvesting antennas[19]. On the contrary, fullerenes and functionalized fullerenes are widely employed as efficient electron acceptors and shoes fragile light absorption as a result of forbidden singlet-singlet electronic transition[20-22]. Due to the consolidating electronic properties, fullerene-porphyrin self-assembled systems are suitably employed in the construction of photosynthetic models and to generation of artificial PET and/ PEnT process(s)[23,24]. Due to versatile characteristic features as

a Department of Chemistry, The University of Burdwan, Golapbag, Burdwan - 713 104, India.

b Department of Computer Science Engineering, Academy of Technology, Adisaptagram, Hooghly, West Bengal - 712 502, India.

c Department of Physics, Academy of Technology, Adisaptagram, Hooghly, West Bengal - 712 502, India.

d Central Library, The University of Burdwan, Golapbag, Burdwan - 713 104, West Bengal, India

* author for correspondence;
E-mail: sbhattacharya@chem.buruniv.ac.in

discussed above, fullerene-porphyrin system find its role as essential component in devising photoelectrical system[25], for the construction of nano composite materials[26] and establishes its potential prospect in pharmaceutical and medical sciences[27].

In very recent past, systems containing porphyrin, C_{60} and pyrene have shown chemical versatility[28]. Utilizing the adsorption phenomenon of porphyrin analogue over the dodecane/water interface, the PET phenomenon in a fullerene-porphyrin system has been established[29]. Moreover, conjugated bridging by way of interfacing in tetrapyridyl C_{60}-porphyrin dimers is shown to be very much effective for exhibiting prominent ultrafast charge separation[30]. In recent past, variation of effect of donor/acceptor size with rate of PET process is well interpretated by Tkachenko *et al*[31].

Therefore, investigations of non-covalent interaction of a functionalized fullerene, e.g., N-methyl fulleropyrrolidine (1) with designed free-base (2) and zinc porphyrin (3) in solution warrants timelyresearch in the context of cited literature as mentioned above. The present paper reports supra molecular binding of 1 (Fig. 1(a)) with 2 (Fig. 1(b)) and 3 (Fig. 1(c)) in 1, 2-dichlorobenzene through the process of self-assembly. The conformation stability and geometric structures of 1-2 and 1-3 systems are predicted by semiempirical calculations in *vacuo*.

Materials and Methods

1 and 2 are obtained from Sigma-Aldrich, USA. 3 is synthesized and the method is described in Scheme 1. UV-vis spectroscopic grade 1,2-dichlorobenzene (DCB) (Merck, India) is used as solvent which provides additional photostability and solubility to both acceptor (here 1) and donors (here 2 and 3). UV-vis spectral investigations are carried out in a UV-2450 model spectrophotometer. Steady state fluorescence spectra of the samples are measured in a Hitachi F-7000 model spectrofluorimeter. For the time correlated single photon counting (TCSPC) measurements, the samples are excited at 374 nm using a nano second diode laser (IBH Nanoled) in an HORIBA Jobin Yvon

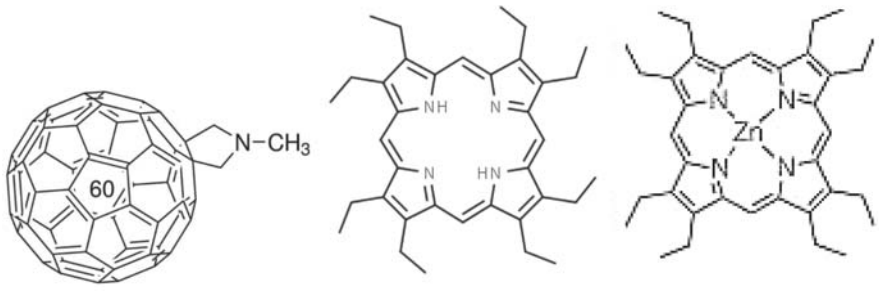


Fig. 1. Structure of (a) **1**, (b) **2** and (c) **3**

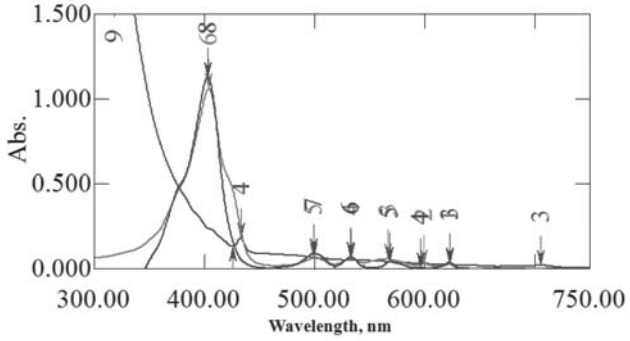


Fig. 2. UV-Vis absorption spectrum of (a) 1 (dark brown color line), (b) 2 (black colour line)and (c) 1-2 system (red colour line) done in DCB and recorded against the solvent as in reference. The concentration of 1 and 2 are maintained at 3.358×10^{-5} mol × dm^{-3} and 4.787×10^{-6} mol×dm^{-3}, respectively, in solution during measurement of absorption spectra.

Single Photon Counting Setup. The typical fwhm of the system response using a liquid scatter is about 200 ps. The repetition rate is 1 MHz. The fluorescence decay curves are analyzed using IBH DAS6 software. Semiempirical third parametric method (PM3) calculations are performed by SPARTAN'14V1.1.0 Windows version software in a Pentium IV computer.

Results and Discussions

UV-vis spectroscopic investigations: Measurements of UV-Vis absorption spectra of uncomplexed 1, uncomplexed 2 and uncomplexed 3 along with 1-2 and 1-3 systems reveal ground state electronic interaction of 1 with 2 and 3 in DCB. The UV-vis spectrum of both 2 and 3 in DCB shows intense absorption spectral features as a result of rich conjugated aromatic system. For 2 and 3, the stronger and the well-resolved absorption bands are visualized in the visible region (ranging from 300 to 650 nm and these bands are defined as Soret (or B) and Q absorption bands. For metalloporphyrin (here 3), B and Q absorption peaks are originated in accordance with the theoretical model provided by Gouterman *et al*.[32,33]. The B and Q absorption peaks in free-base and metalloporphyrin correspond to the vibronic sequence which is resulted by the electronic transition between the ground singlet S_0 to 2nd excited singlet state (S_2) and from the S_0 to 1st excited singlet states (S_1), i.e., $S_2 \leftarrow S_0$ and $S_1 \leftarrow S_0$, respectively. The main absorption peaks of 1 consist in the visible range of two major absorption bands, that is, one at 329 nm and one at 432 nm. The spectral characteristics of 1 (recorded in DCB and measured against the

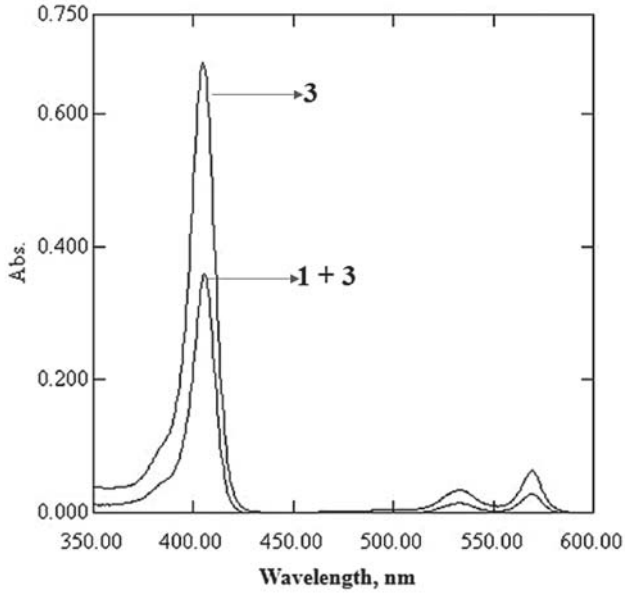


Fig. 3. UV-Vis absorption spectral variation of 3 ($9.40´ 10^{-7}$ mol × dm^{-3})recorded in DCB in absence and presence of 1 ($2.50´ 10^{-5}$mol×dm^{-3}).

solvent as reference) is demonstrated in Fig. 2. Absorption spectrophotometric measurements provide formidable evidence in favour of non-covalent binding between 1 and porphyrins. It is observed that the absorption spectra of both 2 and 3 shows reduction in the value of absorbance at its both Soret and Q absorption bands following the addition of 1. This feature is certainly indicative of complexation between 1 and 2 (/and 3) in DCB. One typical absorption spectral variation of 2 in absence and presence of 1 are shown in Fig. 2. The reduction in the absorbance value of 3 during complexation with 1 is found to be more compared to 2 as evidenced from Fig. 3. This phenomenon indicates stronger binding of 3 with 1 compared to 1-2 system.However, no additional absorption peaks are observed in both the cases observed which is indicative of absence of charge transfer interaction for both 1-2 and 1-3 systems.

Steady State and Time Resolved Fluorescence Studies: To explore the photo induced behavior of 2 and 3 in presence of 1, steady-state fluorescence titration measurements are done in DCB. Fluorescence measurement is very much useful in finding the recognition motif of 1 towards 2 and 3 during supramolecular interaction. Following the gradual addition of fullerene (here 1 is kept at fixed value of concentration) to the solution of porphyrins (here 2 and 3), it is observed that the fluorescence intensity of both 2 and 3 suffers reduction in intensity compared to what observed in absence of 1. The porphyrins are excited at their corresponding Soret ($S_2 \leftarrow S_0$) absorption peak. Typical steady state fluorescence titration experiments for 1-2 and 1-3 systems are nicely demonstrated in Figs. 4(a) & 5(a), respectively. Plot of fluorescence intensity ratio, i.e., (fluorescence intensity of uncomplexed porphyrin/fluorescence intensity of complexed porphyrin) against concentration of the quencher (here 1) originates excellent linear plots for both 1-2 and 1-3 systems as demonstrated in Figs. 4(b) & 5(b), respectively. This observation establishes the occurrence of static quenching mechanism behind the deactivation of the photoexcited porphyrins (here 2 and 3) in presence of 1. In our present work, spontaneous mixing of the individual components, i.e., 1 and porphyrins (i.e., both 2 and 3), form an inter complex superstructure which is very much responsible behind deactivation of the singlet excited state of both2 and 3 in presence of 1. The quenching efficiency (Q) is estimated to be highest in case of 1-3 system (Q = 77%) and it exhibits 6% more quenching efficiency than that measured in case of 1-2 system (Q = 71%). This finding certainly proves strong association between 1 and 3 in solution than that for 1-2 system.Steady state fluorescence investigations elicit the binding constant (K) for the complexes of 1 with 2 and 3 in DCBwith the help of plots as described in Figs. 4(b) & 5(b)[34]. Following correlations are obtained:

For 1-2 system:

$$F_0/F = (0.995 \pm 0.005) + (8740 \pm 265);$$
Correlation Coefficient = 0.99. (1)

For 1-3 system:

$$F_0/F = (0.985 \pm 0.012) + (15590 \pm 735);$$

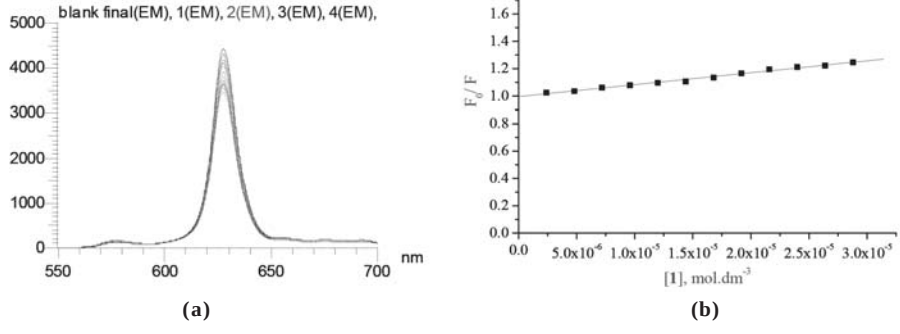


Fig. 4. Steady state fluorescence spectral variation of 2 (4.7868×10^{-6} mol.dm^{-3}) in absence and presence of 1 (2.40×10^{-6} to 3.60×10^{-5} mol.dm^{-3}); (b) Plot of F_0/F vs. concentration of 1 for 1-2 system for the determination of K.

Correlation Coefficient = 0.99. (2)

Table 1. Values of binding constant (*K*, $dm^3.mol^{-1}$) measured from steady state fluorescence measurements and heat of formation (DH_f^0, $dm^3.mol^{-1}$) values for 1-2 and 1-3 systems obtained from semiempirical PM3 calculations in *vacuo*.

Systems	*K*, $dm^3.mol^{-1}$	ΔH_f^0, $dm^3.mol^{-1}$
1-2	8,740 ± 265	19.5
1-3	15590 ± 735	-11.5

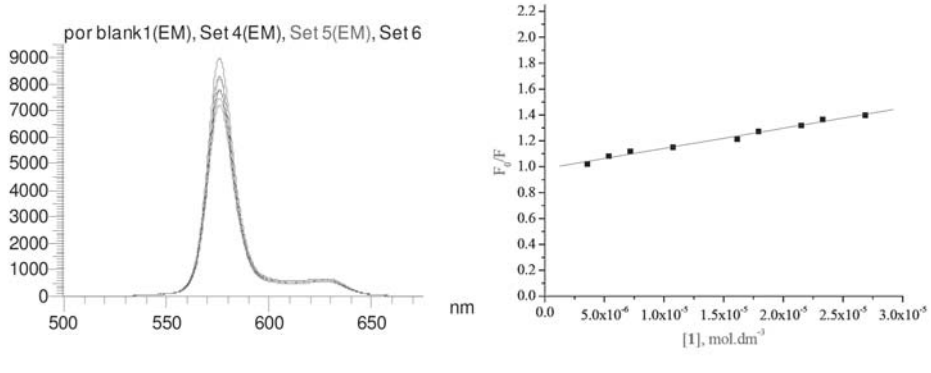
The values of *K* are reported in Table 1. Table 1 reveals high value of *K* for 1-3 system, i.e., $K_{1\text{-}3}$ = 15,590 $dm^3 \times mol^{-1}$ compared to 1-2 system, i.e., $K_{1\text{-}2}$ = 8,740 $dm^3 \times mol^{-1}$. Table 1 also predicts the selectivity in binding between the complex of 1-3 and 1-2, i.e., $K_{1\text{-}3}/K_{1\text{-}2}$ is determined to be ~ 1.80. Although, the selectivity in binding in our present work is estimated to be lower compared to bridged calix[5]arene (~10.2)[35], it shows very much comparable value compared with complex host molecule likeazacalix[m]arene[n]pyridine (~1.9)[36] and that of cyclotriveratrylenophane (~2.5)[37]. However, reported selectivity of binding of *syn*-1 (a designed bisporphyrin) with C_{60} and C_{70} is estimated to be ~ 6.35[38] which is exhibiting ~3.5 times higher value of selectivity in binding compared to that of $K_{1\text{-}3}/K_{1\text{-}2}$ determined in present work.

Apart from steady state fluorescence measurements, a detailed nanosecond time-resolved fluorescence experiments are also performed for the 1-2 and 1-3 systems in DCB using 375 nm laser pulses. The concentration of both 2 and 3 are kept at a fixed value throughout the experiment. In time-resolved fluorescence experiments, both 2 and 3 decay mono-exponentially; the lifetime value of the singlet excited state (τ_0) of 2 and 3 are measured to be 13.95 and 1.65 ns, respectively (listed in Table 2). The

Table 2. Lifetime values of 2 **and** 3**, i.e., in absence (t_0) and presence of** 1 **(**t**) recorded in DCB.**

System	10^5 Concentration of 1, $mol.dm^{-3}$	$10^9 t_0$, ns	t, ns
2	–	**13.95**	
1-2	**1.44**	–	**13.882**
	1.68	–	**13.911**
	1.92	–	**13.868**
	2.15	–	**13.905**
	2.40	–	**13.925**
	2.64	–	**13.833**
	3.35	–	**13.846**
	3.60	–	**13.847**
3	–	**1.65**	
1-3	**1.25**	–	**1.629**
	1.43	–	**1.630**
	1.80	–	**1.624**
	2.15	–	**1.629**
	2.50	–	**1.628**
	2.70	–	**1.624**

decrements in the lifetime value of 2and 3 in presence of 1 are computed to be only 1% for 1-2 and 1-3 systems, respectively, which absolutely supports the rationale of static quenching mechanism behind the photo excited decay of both 2 and 3 in presence of 1. Typical decay curves constructed for 1-2 and 1-3 systems (recorded in DCB) may be visualized in Figs. 6(a) & 6(b), respectively. The notable feature of the lifetime measurements is that in both the cases, no significant decrement in the value of τ_0 is observed even when lifetime titration experiments are performed in DCB. As polarity index of DCB is supposed to be high compared to other solvent like toluene, it may be inferred that there is no possibility of electron transfer mechanism behind the photoexcited decay of 2 and 3 in presence of 1. Moreover,the lifetime experiment rules out existence of any sort of diffusion driven process in present investigations. As the value of τ_0 for both 2 and 3 do not undergo considerable change in presence of the quencher (here 1), there is no chance of getting the lifetime value in different time scale region like picosecond or femtosecond. This



(a) (b)

Fig. 5. Steady state fluorescence spectral variation of 3 (9.40×10^{-7} $mol.dm^{-3}$) in absence and presence of 1 (3.60×10^{-6} to 2.70×10^{-5} $mol.dm^{-3}$); (b) Plot of F_0/F vs. concentration of 1 for 1-3 system for the determination of *K*.

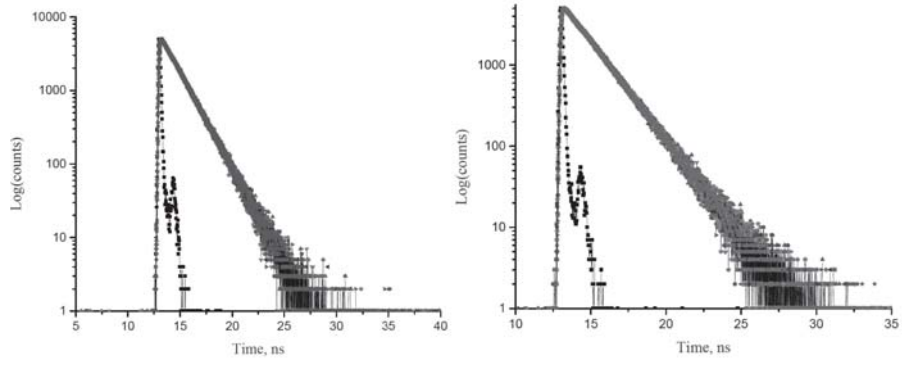
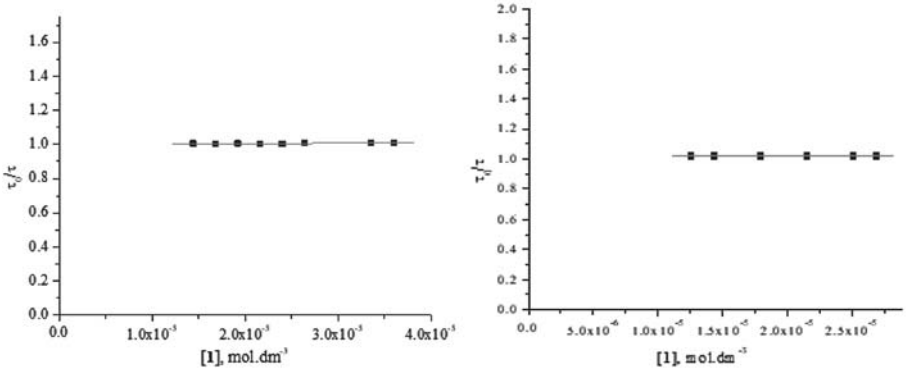
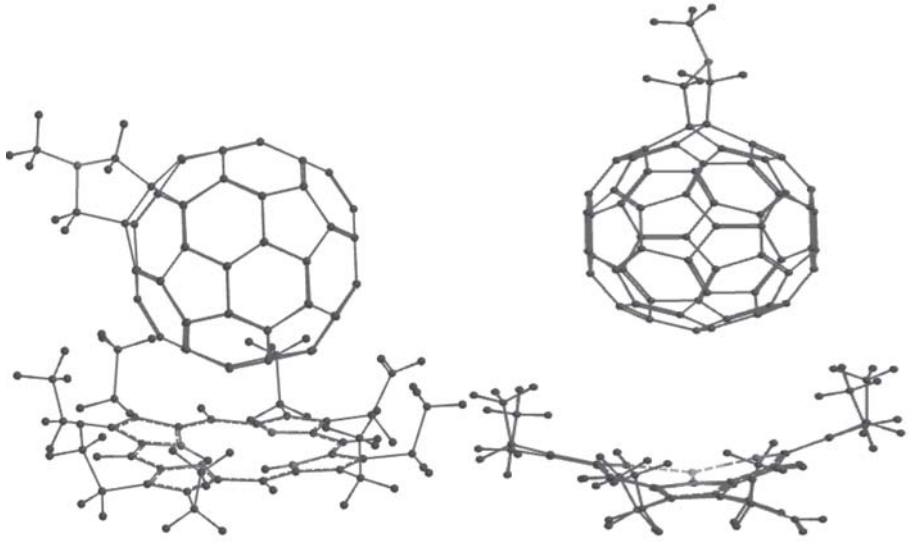


Fig. 6. Decay profile of 2 (4.80 $\times 10^{-6}$ mol.dm ^{3}) and 3 (9.40 $\times 10^{-7}$ mol.dm ^{3}) in presence of 1 (1.25$\times 10^{-5}$ mol.dm^{3} to 3.60 $\times 10^{-5}$ mol.dm^{3}) recorded in DCB.



(a) **(b)**

Fig. 7. SV type plot for (a) 1-2and (b) 1-3 systems done in DCB.



(a) **(b)**

Fig. 8. PM3 optimized geometric structures of (a) 1-2 and (b) 1-3 systems done in *vacuo*.

important finding also supports the view of static quenching mechanism associated with binding phenomena behind the quenching and g of fluorescence of both 2 and 3 in presence of 1 in DCB.

Utilizing the values of τ_0 and t, one important physico chemical parameter, namely, bimolecular quenching constant (k_q) for 1-2 and 1-3 systems have been determined in present work. The value of k_q for 1-2 and 1-3 systems are calculated from K_{SV} with the help of relation $K_{SV} = k_q.\tau_0$, where τ_0 denotes the lifetime of the uncomplexed porphyrins, i.e., 2 and 3 (Fig. 7). The order of k_q for the above mentioned systems is reported to be in the range of 10^{11} which also cancels the occurrence of any diffusion driven process in present work. As diffusion-controlled quenching reaction typically produces k_q value in the order of 10^{10} dm^3 × mol^{-1} × sec^{-1} [39], the reported value of k_q in our present investigations surely indicate binding interaction is the only path behind photo excited decay of 2 and 3 in presence of 1.

Computational Chemistry Calculations: In present investigations, quantum chemical calculations using semiempirical PM3 model generate geometric structure through process of energy minimization. The optimized geometric structures of 1-2 and 1-3 systems are demonstrated in Figs. 8(a) & 8(b), respectively. The substantial binding of 1 with 3 is reflected with less value of heat of formation (ΔH_f^0= -11.5 kcal×mol^{-1}) for this particular complex than that of 1-2 system (ΔH_f^0 = 19.5 kcal×mol^{-1}). Trend in ΔH_f^0 value suggests that 1-3 complex is enthalpically more stable compared to 1-2 complex by 30.0 kcal×mol^{-1}. The above phenomenon affirms that van der Waals attractive forces play significant role in binding interaction between fullerene and porphyrin[40,41]. PM3 calculations also generate molecular electrostatic potential maps (MEPM)

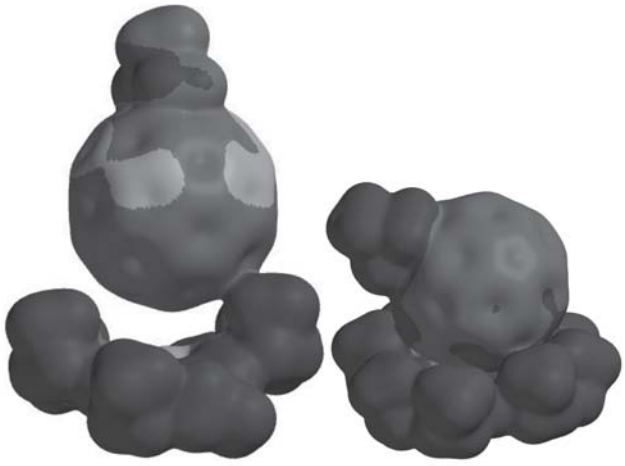


Fig. 9. MEP maps of (a) 1-2 and (b) 1-3 systems done by PM3 calculations in *vacuo*.

for 1-2 and 1-3 systems which are visualized in Figs. 9(a) & 9(b), respectively. Generation and visualization of frontier molecular orbitals and MEPM establish the donor-acceptor type electronic interaction between 1 (here acceptor) and porphyrins (here 2 and 3).

Conclusions

The key features of present work may be summarized as follows:

(1) An effective ground state supramolecular interaction occurs between a functionalized fulleropyrrolidine (here 1) and porphyrins, namely, free-base (2) and zinc porphyrin (3) in DCB.

(2) The interaction is purely in van der Waals type and it is not controlled by any charge transfer type mechanism.

(3) Magnitude of the values of binding constants surmises that 3 (zinc porphyrin) undergoes strong intermolecular interaction with 1 compared to 2 (free-base porphyrin).

(4) Very low selectivity in binding between the complexes of zinc and free-base porphyrin with 1 indicates that the binding is of purely electrostatic in nature.

(5) Both steady state and time resolved fluorescence experiments establish that the photo excited decay of both 2 and 3 in presence of 1 only occurs *via* static quenching mechanism compared to dynamic mechanism.

(6) Optimized geometric structures of 1-2 and 1-3 systems along with the determination of enthalpy of formation values for the above mentioned systems in *vacuo*provide very good support in favour of strong electronic interaction between functionalized fullerene and the porphyrins and moreover, give clear evidence in favour of strong binding of 1 with 3 compared to 2.

(7) Generation of molecular electrostatic potential maps for the 1-2 and 1-3 systems would certainly provide very good perspective for the construction of fulleropyrrolidine based photovoltaic devices in near future.

Acknowledgments

S. Bhattacharya thanks Council of Scientific and Industrial Research (CSIR), New Delhi for providing financial assistance through research project of Sanction No. 01(3083)/21/EMR-II. The authors also wish to record their gratitude to the authority, The University of Burdwan for providing infrastructural facility to SSS, SN and Sumanta Bhattacharya. Shalmali Bhattacharya and Srinjay Bid acknowledge Academy of Technology for giving them the required opportunity to perform the computational work. MB acknowledges the authority of The University of Burdwan for providing basis infrastructural support to her.

Funding Declaration

The present research work gets financial assistance through CSIR sponsored (New Delhi) Research Project having Sanction No. 01(3083)/21/EMR-II.

Conflict of interest

The authors declare no conflict of interest in this work.

Author Contribution

Shiv Sankar Saha and Subrata Nayak have done the major part of the experimental work. The remaining part of the experimental work is done by Prof. Sumanta Bhattacharya. Shalmali Bhattacharya, Dr. Srinjay Bid and Prof. Sumanta Bhattacharya have performed the work of all computational calculations. The art work of the whole paper is done by Miss Moumita Bose. The paper is compiled and written by Prof. S. Bhattacharya. ❐

References

1. G. Suneel, K. Jain, B. Anjaiah, H. Mitra, R.A. Ramnagar, S.

Bandi, V. Chuncha, T.K. Roy, L. Giribabu, R. Chitta, *J. Porphyr. Phthalocyanine*s, **26**: 872-883 (2022).

2. A. Santoro, G. Bella, A.M. Cancelliere, S. Serroni, G. Lazzaro, S. Campagna, *Molecules*, **27**, 2713 **(**2022).
3. X. Yu, B. Wang, Y. Kim, J. Park, S. Ghosh, B. Dhara, R. D. Mukhopadhyay, J. Koo, I. Kim, S. Kim, In-Chul Hwang, S. Seki, D. M. Guldi, Mu-Hyun Baik, K. Kim, *JACS*, **142**, 12596-12601 (2020).
4. S. Hasegawa, S. L. Meichsner, J. J. Holstein, A. Baksi, M. Kasanmascheff, G. H. Clever, *JACS*, **143**, 9718-9723 (2021).
5. N. Armaroli, Photoinduced Energy Transfer Processes in Functionalized Fullerenes, Book Chapter 5 in Fullerenes: From Synthesis to Optoelectronic Properties, 137-162 (2022).
6. M.A. Franco, S.N. Groesser, A Systematic Literature Review of the Solar Photovoltaic Value Chain for a Circular Economy, **13**, 9615 (2021).
7. F.H. Alharbi, S. Kais, *Renew. Sustain. Ener. Rev*. **43**, 1073-1089 (2015).
8. G. Bottari, G.D.L. Torre, T. Torres, *Chem. Rev*. **110**, 6768-6816 (2010).
9. V. Nilolaou, A. Charisiadis, C. Stangel, G. Charalambidis, A. G. Coutsolelos, *C*, **5**, 57 (2019).
10. C. Caballero, J. Calbo, J. Arago, P.D.L. Cruz, E. Orti, N.V. Tkachenko, F. Langa, *J. Mat. Chem. C*, **9**, 10889-10898 (2021).
11. A. Ray, S. Bhattacharya, *J. Mol. Liq*. **254,** 291-303 (2018).
12. Y. Xu, B. Wang, M.B. Minameyer, M. Bothe, T. Drewello, D.M. Guldi, M.V. Delius, *Angew. Chem. Int. Ed*. **57**, 11549–11553 (2018).
13. A. Ray, S. Banerjee, S. Ghosh, A.K. Bauri, S. Bhattacharya, *Spectrochim. Acta Part A*, **152**, 64-69 (2016).
14. A. Ray, S. Banerjee, A.K. Bauri, S. Bhattacharya, *Chem. Phys. Lett*. **646**, 119-124 (2016).
15. D.V. Konarev, S.S. Khasanov, R.N. Lyubovskaya, *Coord. Chem. Rev*. **262**, 16–36 (2014).
16. A. Ray, A. Bauri, S. Bhattacharya, *Spectrochim. Acta Part A*, **134**, 566-573 (2015).
17. B.K. Ghosh, A. Bauri, S. Bhattacharya, S. Banerjee, *Spectrochim. Acta Part A*, **125**, 90-98 (2014).
18. S. Fukuzumi, K. Ohkubo, T. Suenobu, *Acc. Chem. Res*. **47**, 1455–1464 (2014).
19. J. Otsuki, *J. Mater. Chem. A*, **6**, 6710-6753 (2018).
20. Y. Hashikawa, S. Sadai, S. Okamoto, Y. Murata, *Angew. Chem. Int. Ed*. **62**, e202215380 (2023).
21. S. Bhattacharya, S.K. Nayak, S.K. Chattopadhyay, M. Banerjee, A.K. Mukherjee, *Spectrochim. Acta Part A*, **57**, 309-313 (2001).
22. Lecture Notes on Fullerene Chemistry: A Handbook for Chemists, R. Taylor, World Scientific, Pages: 288 (1999).
23. M.J. Llansola-Portoles, D. Gust, T.A. Moore, A.L. Moore, *Comptes. Rendus. Chimie*. **20**, 296-313 (2017).
24. L.A. Frolova, Y. Furmansky, A.F. Shestakov, N.A. Emelianov, P.A. Liddell, D. Gust, I. Visoly-Fisher l, P.A. Troshin, *ACS Appl. Mater. Interfaces*, **14**, 15461–15467 (2022).
25. A.J. Stasyuk, O.A. Stasyuk, M. Solà, A.A. Voityuk, *Chemistry A European Journal*, **25** 2577-2585 (2019).
26. A. Kausar, I. Ahmad, M. Maaza, M.H. Eisa, P. Bocchetta, *J. Compos. Sci*. **6**, 393 (2022).
27. J.L. Sessler, N.A. Tvermoes, J. Davis, P. Anzenbacher, K. Jursíková, W. Sato, D. Seidel, V. Lynch, C. Black, A. Try, Pure Appl. Chem. **71**, 2009-2018 (1999).
28. P. Porcu, A.S. Estrada-Montaño, M. Vonlanthen, F. Cuétara-Guadarrama, I. González-Méndez, K. Sorroza-Martínez, G. Zaragoza-Galán, E. Rivera, *Dyes and Pigments*, **197**, 109858 (2022).
29. J. Sissaoui, A. Efimov, T. Kumpulainen, E. Vauthey, *J. Phys. Chem. B*, **26**, 4723-4730 (2022).
30. C. Stangel, F. Plass, A. Charisiadis, E. Giannoudis, G. Chararalambidis, K. Karikis, G. Rotas, G.F. Zervaki, N.N. Lathiotakis, N. Tagmatarchis et al. *Phys. Chem. Chem. Phys*. **20**, 21269–21279 (2018).
31. N.V. Tkachenko, *Photochem*. **2**, 918–931 (2022)**.**
32. D. Eastwood, M. Gouterman, *J. Mol. Spectroscopy*, **23**, 210-212 (1967).
33. A.M. Schaffer, M. Gouterman, E.R. Davidson, *Theor. Chim. Acta*, **30**, 9-30 (1973).
34. Principles of Fluorescence Spectroscopy, J.R. Lakowicz, Springer, (2006).
35. T. Haino, M. Yanase, Y. Fukazawa, *Angew. Chem. Int. Ed*. **3,** 997-998 (1998).
36. Mei-Xiang Wang, Xiao-Hang Zhang, Qi-Yu Zheng, *Angew. Chem. Int. Ed*. **43**, 838-842 (2004).
37. H. Matsubara, S. Oguri, K. Asano, K Yamamoto, *Chem. Lett*. 431-432 (1999).
38. P. Mukherjee, S. Chattopadhyay, S. Bhattacharya, *J. Porphyr. Phthalocyanine*, **16**, 14-24 (2012).
39. F. D'Souza, O. Ito, *Chem. Commun.* 4913–4928 (2009).
40. Yi–Bo Wang, Z. Lin, *JACS*, **125**, 6072-6073 (2003).
41. T. Karilainen, O. Cramariuc, M. Kuisma, K. Tappura, *J. Computational Chem.* **36**, 612-621 (2015)