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Short Communication

PyC₆₀-naphthacrown system: A new supramolecular recognition element

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- PyC₆₀-naphthacrown (1) noncovalent interaction is established in solution.
- Magnitude of binding constant of PyC_{60} -1 system is estimated to be 58,300 dm³ mol⁻¹.
- Photo-excited decay of **1** in presence of PyC₆₀ takes place through static quenching.
- Solvent reorganization energies indicate energy transfer upon photoexcitation.

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Introduction

The search for proper macrocyclic receptors with complimentary sites for efficient binding of fullerenes is gaining current impetus [1–4]. An interesting aspect of the chemistry of fullerenes and various macrocyclic receptors is that they are spontaneously attracted to each other, as a result of ground state complexation. Among all the receptors reported so far, porphyrin [5–9] and

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ABSTRACT

Fulleropyrrolidine (PyC₆₀) and a binaphthyl bridged crown ether macrocyclic receptor (1) undergoes spontaneous self-assembly phenomenon in solution to generate a new supramolecular recognition element having binding constant value of \sim 5.83 × 10⁴ dm³ mol⁻¹. Lifetime measurement reveals a static quenching mechanism behind the deactivation of photoexcited state of 1 in presence of PyC₆₀. The results obtained from this work would definitely reinforce bridged cyclic crown ether as one of the most suitable fragments for the molecular recognition of various macrocyclic receptor(s) in near future.

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phthalocyanine (Pc) [10–14] occupy the major part of the literature in terms of their unique binding motif as well as appealing photophysical properties. An Ir(III) metalloporphyrin demonstrates the highest value of binding constant (*K*), i.e., $K = 1.25 \times 10^8$ dm³ mol⁻¹, with C₆₀ measured in 1,2-dichlorobenzene [15]. It is already reported that both C₆₀ and C₇₀ form ground state molecular complexes with naphthalene [16] and crown ether [17,18] as a result of formation of electron donor–acceptor (DA) or charge transfer (CT) complex. However, the estimated *K* values for the fullerene– naphthalene and fullerene–crown ether complexes are not so significant in comparison to what fullerene exhibits with other host

molecule as mentioned above. For example, the K values for the C_{60} -naphthalene and C_{70} -naphthalene complexes are determined to be only 0.4 [16] and 0.2 $dm^3 mol^{-1}$, [16] respectively. Similarly, the K values for the electron donor-acceptor complexes of C₆₀-benzo-15-crown-5 and C₇₀-benzo-15-crown-5 complexes are estimated to be 641 and 116 dm³ mol⁻¹, respectively [17,18]. As a result of this, the design of macrocyclic receptor molecule having naphthalene based crown ether moiety (1, Scheme 1) would be of potential interest to examine its binding affinity and photophysical properties in presence of fullerene derivative, e.g., C₆₀ pyrrolidine tris-acid ethyl ester (PyC_{60}) (Scheme 2). The design of the macrocyclic receptor **1** conserves the basic feature of the propeller shaped crown receptor but includes binaphthyl bridged alkyl linker. We envisaged that this sort of study is expected to provide information about the formation of supramolecular architecture which spans from the nanoscopic to the macroscopic level across multiple length scales, and affect the intermolecular binding strength between 1 and fullerene because of different wave-function mixing in the non-covalently linked DA pair.

Materials and methods

Synthesis of macrocyclic naphthacrown **1** starts with the acid catalyzed (CSA) condensation of 2-naphthol with benzaldehyde to afford *bis*-naphthol **1**a in good yield. The compound **1** was finally achieved by the alkylation of **1**a with pentaethyleneglycol ditosylate. No dimeric product was isolated. Detailed synthetic procedure is delineated below.





Scheme 2.

Synthesis of 1a

A mixture of 2-naphthol (1.44 g, 10 mmol), benzaldehyde (0.584 g, 5.5 mmol) and (±)-camphor-10-sulfonic acid (CSA, 0.232 g, 1.0 mmol) was stirred in dry acetonitrile at ambient temperature (25 °C). After 16 h of reaction, TLC indicated complete consumption of both the starting materials. The synthesized material was filtered followed by washing with water and dried in air. The crude solid was recrystallized with hexane-ethyl acetate solvent mixture to afford pure 1a (1.41 g, 75%), a pink colored solid; mp 195-196 °C; IR (CHCl₃): v 3471, 3423, 3019, 1618, 1597, 1513, 1491, 1468, 1390, 1253, 1046, 877 cm⁻¹; ¹H NMR (200 MHz, CD₃COCD₃): δ 7.13-7.38 (m, 12H, ArCHAr, ArH), 7.74-7.84 (m, 4H, ArH), 8.12 (d, *J* = 8.3 Hz, 2H, ArH); ¹³CNMR (50 MHz, CD₃COCD₃): δ 43.0, 120.1, 120.4, 123.6, 123.7, 126.8, 127.5, 128.8, 129.1, 129.7, 130.0, 130.5, 135.2, 143.3, 154.0; MS, m/z (%) = 376 (M, 25), 375 (95), 353 (8), 349 (11), 339 (16), 337 (10), 325 (10), 321 (100), 311 (11), 309 (16), 293 (22), 283 (9), 265 (16), 231 (58), 143 (39); HRMS: *m*/*z* calc. for C₂₇H₂₀O₂Na (M + Na): 399.1361; found: 399.1365 (see Supporting Information).

Synthesis of 1

A mixture of bis-(2-naphthol) 1a (0.790 g, 2.1 mmol), pentaethyleneglycol ditosylate (1.26 g, 2.3 mmol, 1.1 equiv) and Cs₂CO₃ (1.73 g, 5.3 mmol, 2.5 equiv) was refluxed in dry acetonitrile (30 ml) for 8 h. TLC experiment revealed absence of both 1a and the ditosylate. The solvent was then removed under vacuo, and allowed to cool in room temperature; the reaction is then quenched with 1 N HCl and extracted with ethyl acetate. The organic layer was washed with water, brine and dried (Na₂SO₄) in a sequential manner. Removal of solvent afforded a thick mass which was purified by silica gel column chromatography (using CHCl₃ as eluant) to afford pure 2 (0.948 g, 78%), a light vellow colored solid having mp 155-156 °C; IR (CHCl₃): v 3058, 3016, 2874, 1622, 1598, 1511, 1492, 1451, 1295, 1259, 1243, 1215, 1176, 928, 806, 697 cm⁻¹; ¹H NMR (200 MHz, CDCl₃): δ 2.88–2.98 (m, 2H, OCH2CH2O), 3.10-3.21 (m, 2H, OCH2CH2O), 3.31-3.35 (m, 4H, $2 \times OCH_2CH_2O$), 3.45–3.48 (m, 8H, $4 \times OCH_2CH_2O$), 3.69–3.71 (m, 2H, OCH₂CH₂O), 3.77-3.83 (m, 2H, OCH₂CH₂O), 7.03-7.14 (m, 6H, ArCHAr, ArH), 7.23-7.30 (m, 6H, ArH), 7.73-7.81 (m, 6H, ArH); $^{13}\text{CNMR}$ (50 MHz, CDCl3): δ 43.9, 68.4, 68.9, 70.3, 116.1, 122.7, 124.0, 124.8, 125.2, 125.8, 127.5, 128.1, 128.2, 128.7, 129.4, 133.4, 144.9, 155.2; MS, m/z (%) = 578 (M, 100), 577 (43), 259



Fig. 1. Steady state UV-vis titration experiment of **1** (at a fixed concentration of 8.65×10^{-6} mol dm⁻³) in presence of variable concentration of PyC₆₀ (6.7×10^{-6} to 4.5×10^{-5} mol dm⁻³) at 298 K; the inset of figure shows UV-vis BH plot. $\lambda_{obs} = 430$ nm. The bottom black and green lines represent UV-vis spectrum of uncomplexed **1** and PyC₆₀, respectively, recorded in toluene. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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Fig. 2. Steady state fluorescence spectral variation of **1** (8.65 × 10⁻⁷ mol dm⁻³) in presence of PyC₆₀ (2.45 × 10⁻⁶ to 3.45 × 10⁻⁵ mol dm⁻³) recorded in toluene at 298 K; the inset of figure shows modified fluorescence BH plot. λ_{ex} = 337 nm; λ_{em} = 365 nm.

Table 1

Binding constant (K) of PyC₆₀-**1** system done by steady state UV-vis and fluorescence investigations in toluene along with the average value of K. Temp. 298 K.

System	K, dm ³ mol ⁻¹		$K_{\rm av}$, dm ³ mol ⁻¹	
	UV-vis	Fluorescence		
РуС ₆₀ -1	61,950	54,660	~58,300	



Fig. 3. Time-resolved fluorescence decay profile of (a) **1** ($5.45 \times 10^{-6} \text{ mol dm}^{-3}$) in presence of (b) PyC₆₀ ($6.25 \times 10^{-5} \text{ mol dm}^{-3}$) recorded in toluene at 298 K; λ_{ex} = 337 nm; λ_{decay} = 365 nm.

(35), 171 (31), 169 (25); HRMS: m/z calcd. for $C_{37}H_{39}O_6$ (M + H): 579.2747; found: 579.2731; anal. calc. for $C_{37}H_{38}O_6$: C, 76.79; H, 6.62%. Found: C, 76.96; H, 6.51% (see Supporting Information).

The fullerene derivative, e.g., PyC_{60} (shown in Scheme 2) is obtained from Aldrich, USA and used after checking the purity of the compound. The purity of the material has been checked in accordance with the work done by Isacs and Diederich [19]. The motivation behind selecting the PyC_{60} molecule as an electron acceptor comes from the work of Sessler et al. in which they have employed fulleropyrrolidine bearing a guanosine moiety as a recognition motif for the construction of C_{60} -Pc dyad system [20]. HPLC grade toluene (Merck, Germany) is used as solvent to favor non-covalent interaction between PyC_{60} and **1** and, at the same time, to ensure good solubility and photo-stability of the samples. Job type: Geometry optimization.

Method: RHF; Basis set: STO-3G; Number of shells: 301; Number of basis functions: 667

Multiplicity: 1

SCF model:

A restricted Hartree-Fock SCF calculation has been performed using Pulay DIIS + Geometric Direct Minimization

Optin	nization:		
Step	Energy	Max Grad.	Max Di
1	-5050.201969	0.045343	0.04982
2	-5050.241354	0.030271	0.04569
3	-5050.256934	0.023523	0.06332
4	-5050.261119	0.021064	0.06237
5	-5050.263332	0.019731	0.06523
6	-5050.264862	0.019111	0.06774
7	-5050.266131	0.019078	0.06605
8	-5050.267141	0.019143	0.06547
9	-5050.267920	0.019369	0.07033
10	-5050.268520	0.019444	0.06267
11	-5050.269030	0.019421	0.11757
12	-5050.269444	0.019205	0.05001
13	-5050.269805	0.018650	0.17062
14	-5050.270138	0.017739	0.09766
15	-5050.270517	0.016843	0.15753
16	-5050.270980	0.016036	0.07991
17	-5050.271403	0.015174	0.08736
18	-5050.271818	0.014232	0.04691
19	-5050.272225	0.012530	0.04413
20	-5050.272594	0.009517	0.05720
21	-5050.272867	0.006163	0.03211
22	-5050.273065	0.004459	0.05086
23	-5050.273245	0.003714	0.03529
24	-5050.273397	0.003201	0.05416
25	-5050.273525	0.002817	0.03135
26	-5050.273652	0.002894	0.04852
27	-5050.273789	0.002879	0.03634
28	-5050.273919	0.003118	0.03482
29	-5050.274049	0.002927	0.04149
30	-5050.274165	0.002929	0.03775
31	-5050.274278	0.002829	0.04032
32	-5050.274405	0.002674	0.06285
33	-5050.274533	0.002599	0.04527
34	-5050.274642	0.002679	0.04790
35	-5050.274740	0.002685	0.03337
36	-5050.274812	0.002819	0.02435
37	-5050.274878	0.002738	0.03118
38	-5050.274952	0.002523	0.03664

Scheme 3.

UV-vis spectral measurements are performed on a Shimadzu UV-2450 model spectrophotometer using quartz cell with 1 cm optical path length. Emission spectra have been recorded with a

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39	-5050.275027	0.002211	0.050540				
40	-5050.275096	0.002290	0.042741				
41	-5050.275152	0.002766	0.051204				
42	-5050.275193	0.002952	0.049638				
43	-5050.275228	0.003114	0.087615				
44	-5050.275265	0.003251	0.110031				
45	-5050.275303	0.003308	0.134577				
46	-5050.275341	0.003492	0.126616				
47	-5050.275380	0.003489	0.098317				
48	-5050.275418	0.003399	0.096945				
49	-5050.275452	0.003121	0.098085				
50	-5050.275484	0.002680	0.112027				
51	-5050.275512	0.002260	0.110388				
52	-5050.275534	0.001834	0.117449				
53	-5050.275552	0.001499	0.101228				
54	-5050.275568	0.001088	0.090044				
55	-5050.275583	0.001011	0.048023				
56	-5050.275597	0.000792	0.027774				
57	-5050.275608	0.000603	0.107712				
58	-5050.275610	0.000510	0.033548				
59	-5050.275614	0.000488	0.039305				
60	-5050.275619	0.000394	0.030301				
61	-5050.275622	0.000480	0.025238				
62	-5050.275625	0.000371	0.019542				
63	-5050.275628	0.000350	0.038229				
64	-5050.275631	0.000326	0.047463				
65	-5050.275634	0.000361	0.027815				
66	-5050.275637	0.000389	0.035002				
67	-5050.275640	0.000469	0.020973				
68	-5050.275643	0.000493	0.025605				
69	-5050.275646	0.000506	0.034947				
70	-5050.275649	0.000483	0.027593				
71	-5050.275651	0.000442	0.020003				
72	-5050.275653	0.000378	0.010493				
73	-5050.275655	0.000343	0.003711				
74	-5050.275656	0.000298	0.006220				
75	-5050.275657	0.000294	0.005214				
76	-5050.275658	0.000282	0.005810				
Reason for exit: Successful completion							
Quant	um Calculation CPU Time : 1	4:37:50.50					
Quantum Calculation Wall Time: 45:29:01.37							

Scheme 3 (continued)

steady state Hitachi F-7000 model spectrofluorimeter. Fluorescence decay curves are measured with a HORIBA Jobin Yvon single photon counting set up employing nanoled as excitation source. PyC_{60} is selectively excited by 532 nm light from a Nd:YAG laser (6 ns fwhm) with 7 mJ power. For the transient absorption spectra in the visible region, a photomultiplier tube has been used as a detector for the continuous Xe-monitor light (150 W). Theoretical calculations are performed using Gaussian '03 and SPARTAN'06 V1.1.0 (USA) Windows version software.

Results and discussions

Binding studies by UV-vis absorption and steady state fluorescence techniques

It is observed that both PyC_{60} and **1** attract each other spontaneously in toluene and the binding constant (*K*) of PyC_{60} -**1** system is determined to be 61,950 dm³ mol⁻¹ as evidenced from UV-vis investigations (Fig. 1). The *K* value of PyC_{60} -**1** system gets further support from steady state fluorescence measurements (Fig. 2); *K* of PyC_{60} -**1** system (see Table 1) is evaluated employing modified Benesi–Hildebrand equation in both UV-vis and fluorescence experiments [21]. An excellent straight line plot is obtained with correlation factor of 0.99 (inset of Figs. 1 and 2). The average value of *K*, viz., K_{av} for the PyC_{60} -**1** system is estimated to be 58,300 dm³ mol⁻¹. Noteworthy is that, PyC_{60} -**1** system is reported to exhibit ~91.0 times higher magnitude of *K* (as reported in Table 1) compared to C_{60} -benzo-15-crown-5 system [17].

Time-resolved fluorescence study

Apart from steady state fluorescence measurements, we have performed detailed nanosecond time-resolved fluorescence experiment for PyC_{60} -1 supramolecule. The experiment has been



Fig. 4. Ab initio optimized geometric structure of PyC₆₀-1 system done in vacuo.

carried out at a fixed concentration of **1**. The time-resolved fluorescence measurement shows mono-exponential decay for uncomplexed **1**; life time value of the singlet excited state (τ^{s}) of **1** is measured to be 6.0 ns Fig. 3(a). In presence PyC₆₀, however, no significant amount of quenching in the τ^{s} value of **1** (5.95 ns) has been observed and decay follows mono-exponential pathway Fig. 3(b). Lifetime measurement, therefore, suggests a static quenching mechanism behind the deactivation of photoexcited state of **1** in presence of PyC₆₀.

Theoretical calculations

In our present study, we have done exclusive density functional theoretical (DFT) calculations (single point) with the help of restricted B3LYP method using 6-31G(D) basis set in vacuo. Before energy calculations, we have optimized the geometry of PvC_{60} -1 complex by ab initio calculations using STO 3G basis set. Detailed optimization steps are given as Scheme 3. The DFT calculations confirm very good fitting of the PyC₆₀ molecule with the plane of **1**. The heat of formation value of the PyC_{60} -**1** complexation process is enumerated to be 4.35 kcal mol⁻¹. Single projection geometric structure of the PyC₆₀-1 system, optimized by *ab initio* calculation in vacuo, is depicted in Fig. 4. The most significant observation in Fig. 4 is that during complexation, the electron deficient part of unsubstituted C_{60} , is pointed towards the cavity of **1** keeping the electron rich functionalized part (i.e., pyrrolidine unit) in opposite space of **1**. This particular binding motif of PyC₆₀ towards **1** envisage that electrostatic interactions originating from the electron density at the surface of the PyC_{60} and 1 are supposed to play vital role in our present work. The existence of the electrostatic interactions between fullerene and 1 have been evidenced by the results obtained on frontier molecular orbitals, viz., highest occupied molecular orbital (HOMO) and lowest unoccupied molecular

orbital (LUMO). DFT calculations reveal that, in the ground state, the HOMO is exclusively located on **1**, while the LUMO is precisely positioned in fullerene entity of the complex (Fig. 5); this observation evokes that **1** and PyC_{60} act as donor and acceptor, respectively. The absence of HOMO on fullerene and LUMO on 1 also suggests absence of charge transfer (CT) interaction between 1 and fullerene, which is consistent with the fact that no CT bands are observed for PyC₆₀-1 supramolecule in the UV-vis experiment as mentioned earlier. Moreover, in all the cases studied, the position of the LUMO + 1 to LUMO + 6 states are exclusively found on the fullerene unit (see Supporting Information). If we look into detail regarding feature of HOMO, it is observed although HOMO - 1 is precisely centered on naphthacrown unit, HOMO - 2, HOMO - 3 and HOMO - 4 are positioned on fullerene (see Supporting Information). Molecular electrostatic potential (MEP) maps have been generated for PyC_{60} (see Supporting Information), 1 (see Supporting Information) and PyC₆₀-1 (Fig. 6) system in vacuo. Interestingly, in the supramolecular complex, the original deep reddish-green color of the separated PyC₆₀ has been changed to pale reddish yellow color, and deep blue color of **1** is changed to bluish green, indicating strong propensity of electrostatic interaction between these two chromophores upon photo-excitation. The DA distance (r_{DA}) , viz., 3.090 Å (H40 of **1**, Bond191 of PyC₆₀) estimated by DFT calculations also supports strong association between PyC₆₀ and **1** during complexation. Utilizing the value of r_{DA} , the solvent reorganization energy (R) [22] of the PyC₆₀-1 system is estimated to be -0.815 eV. R of PyC₆₀-1 system exhibits higher value compared to fullerene-diporphyrin system [23] and very much comparable with PyC₆₀-Pc systems reported in recent past. The magnitude of R, however, does not indicate possibility of electron transfer mechanism behind photoactive decay of 1 in presence of PyC₆₀ and rather indicative of photoinduced energy transfer process [24,4,25].



Fig. 5. (a) HOMO and (b) LUMO of PyC₆₀-1 system done in vacuo along with schematic diagram of orbital energies at various electronic states.

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Fig. 6. MEP of PyC_{60} -1 system done in *vacuo* by DFT/B3LYP/6-31G(d) calculations in *vacuo*.

Conclusions

In summary, we have described a binaphthyl bridged crown ether macrocyclic receptor that associates fulleropyrrolidine effectively with a *K* of 10^4 orders of magnitude. The magnitude of solvent reorganization energy indicates propensity of electron transfer mechanism behind photoactive decay of **1** in presence of PyC₆₀. The results emanating from this work would definitely reinforce bridged cyclic crown ether as one of the most suitable fragments for the molecular recognition of various macrocyclic receptor(s) in near future.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2014.09.020.

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