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Synthesis, photophysical and electrochemical properties of a new class of fluorescent amidoanthracenophanes

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Abstract

Fluorescent amidoanthracenophanes **1**, **2**, **3** and **4** were obtained from the various aromatic diacidchlorides and diamino precyclophane by simple acylation. All the synthesized amidoanthracenophanes **1**, **2**, **3** and **4** show three intense fluorescent bands between 401-402, 426-429 and at 449-451 nm exhibit two/ three oxidation reduction peaks in the cyclic voltammetry which is characteristic of fluorophoric anthracene unit.

Keywords: Amide, Anthracene, acid chloride, cyclic voltammogram, cyclophane

Introduction

Design and synthesis of new class of photoactive cyclophanes¹ with intraannular amide and anthracene functionality and with various aromatic spacer units are of interest during recent years. Such cyclophanes have potential applications in supramolecular chemistry due to their high degree of structural rigidity and are known to form unusually strained molecules, which can be used for the recognition of specific guest molecules,² and in molecular electronic machines,³ and as drug carriers,⁴ and catalysts in organic synthesis.⁵ Such cyclophanes have rigid structure with well defined non collapsible cavity, which influence the encapsulation of specific guest molecules by non-covalent interactions,⁶ host-guest complexation,⁷ molecular self-assembly, and specific receptor⁸ activity. Anthracene based hybrids⁹ have enormous photoactive applications in the field of material chemistry as well as in biological chemistry. Anthracene is an important building block to develop blue

luminescent dyes due to its merits such as the thermal and electrochemical stability.¹⁰ OLEDs have attracted enormous attention from the scientific community due to their high technological potential for the next generation of full-color-flat-panel displays¹¹ and light emitting applications.¹² with excellent stability¹³ Many kinds of anthracene-functionalized materials have been synthesized and considered for such applications,¹⁴ and some of them were found to be promising blue emitters for OLEDs¹⁵ and also function as blue-light-emitting and hole-transporting materials.¹⁶ Non-doped blue OLEDs with a maximum efficiency of 1.65 cdA⁻¹ were attained using anthracene moiety.¹⁷ The anthracene hybrid molecules shows strong luminescent behaviour and have been widely used as blue-emitting materials in OLEDs due to their excellent photoluminescence (PL) and electroluminescence (EL) properties. Anthracene based compounds are used for intramolecular charge transfer (CT) fluorescence¹⁸ and for sensing metal ion such as Fe²⁺, alkali, alkali earth and heavy metal ions as well as anions such as F⁻, Cl⁻ and Br⁻.¹⁹ Anthracene based cyclophanes can sense Pyrophosphate ion (PPi)²⁰ which is involved in many vital metabolic and bioenergetic processes such as DNA and RNA polymerization and for ATP hydrolysis²¹ and as light active protein cleaving agents²² and further they can be used in fuel cells, and as biomimetic catalysts and in efficient light harvesting antenna devices.

Though we have reported from our lab the synthesis and selective ion separation of various biologically useful amide cyclophanes,²³ the preparation of new class of cyclophanes called amidoanthracenophanes remain unexplored. We wish to report the synthesis, photophysical and electrochemical properties of new class of cyclophanes **1**, **2**, **3** and **4** referred as amidoanthracenophanes (Fig. 1).

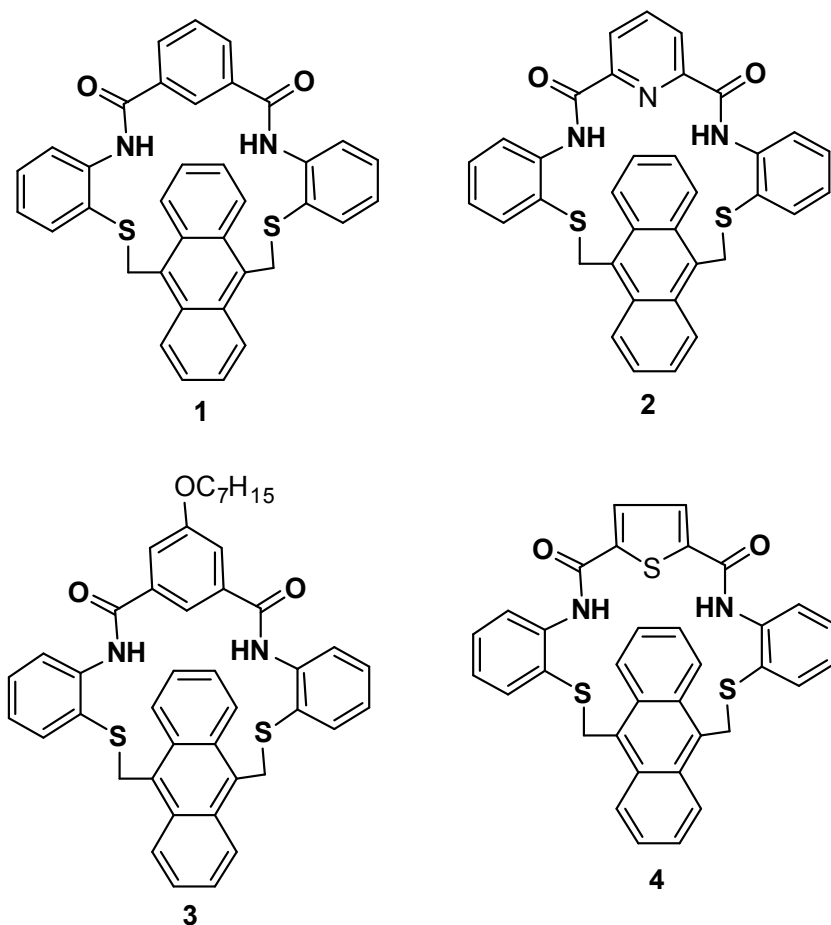
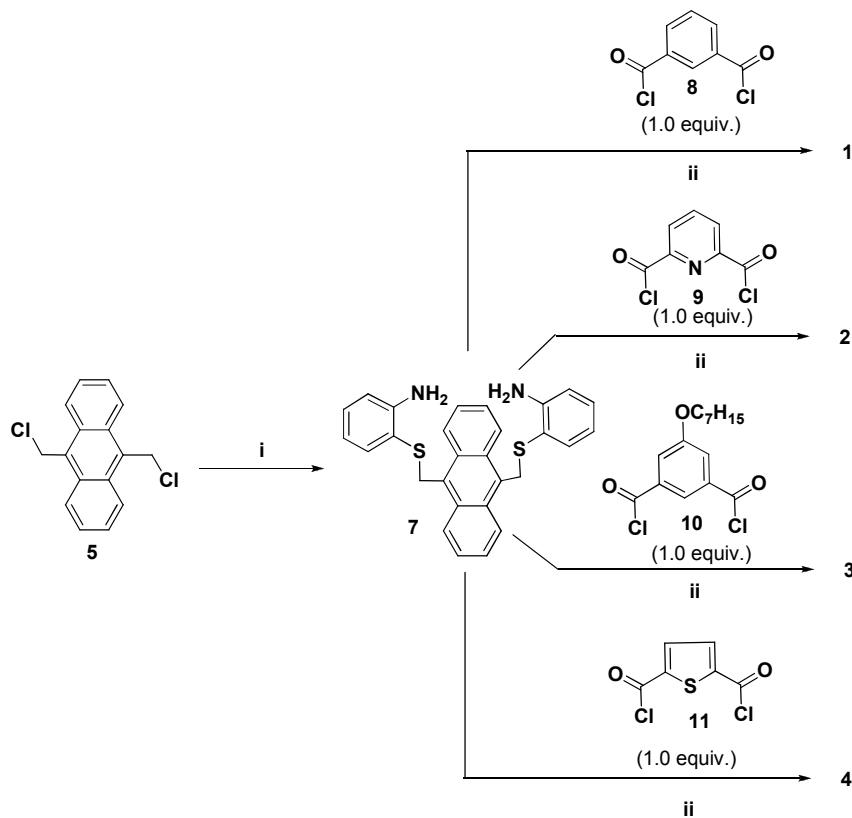


Fig. 1. Structure of new class of cyclophanes **1**, **2**, **3** and **4** called amidoanthracenophanes

Result and discussions

Synthesis of amidoanthracenophanes **1**, **2**, **3** and **4** begins from the reaction of 2-aminobenzenethiol **6** with 9, 10-chloromethyl anthracene **5** in the presence of KOH and catalytic amount of TBAB (10 mg) in a mixture of toluene/ H₂O (1:1) to give the precyclophane diamine **7** in 86% yield (scheme 1). The ¹H NMR spectrum of precyclophane diamine **7** displayed a broad singlet at δ 4.33 for amine protons, a singlet at δ 4.93 for *S*-CH₂ protons in addition to the signals for aromatic protons. In the ¹³C NMR spectrum, precyclophane diamine **7** showed the *S*-CH₂ carbons at δ 32.9 in addition to the signals for aromatic carbons. The mass spectrum (ESI-MS) of precyclophane diamine **7** showed the molecular ion peak at *m/z* 542. Further, the structure of the precyclophane diamine **7** was also confirmed from elemental analysis.



Scheme 1 Reagents and conditions: (i) 2-aminothiophenol **6** (2.1 equiv.) KOH, TBAB (cat), toluene-H₂O, 12 h, **7** (86%); (ii) TEA, DCM (dry), 15 h, **1** (62%), **2** (63%) **3** (62%) and **4** (64%).

The diacid chlorides **8**, **9**, **10** and **11** were prepared from the corresponding dicarboxylic acid using thionyl chloride (SOCl₂) as per the reported procedure.²⁴ The fluorescent amidoanthracenophanes **1**, **2**, **3** and **4** were synthesized in 62%, 63%, 62% and 64% yields, respectively by the reaction of 1 equiv. of precyclophane diamine **7** with 1 equiv. of isophthaloyl chloride **8**/ 2,6-pyridine dicarboxylic acid chloride **9**/ 5-n-heptyloxy isophthaloyl chloride **10**/ 2,5-thiophene dicarboxylic acid chloride **11** in the presence of dry DCM, TEA under nitrogen atmosphere for 15 h at room temperature. In ¹H NMR spectrum, amidoanthracenophane **2** exhibited a sharp singlet at δ 4.96 for *S*-CH₂ protons and a singlet at δ 9.06 for the amide NH protons in addition to the aromatic proton signals. The ¹³C NMR spectrum of amide cyclophane **2** showed *S*-CH₂ carbon at δ 34.5 and amide carbonyl carbon at δ 160.9 in addition to the signals for the aromatic carbons. The mass spectrum (ESI-MS) of

2 showed the molecular ion peak at m/z 583 (M^+). Further, the structure of the amide cyclophane **2** was also confirmed from elemental analysis.

In the ^1H NMR spectrum, the fluorescent amidoanthracenophane **3** showed triplet at δ 0.90 for the alkyl methyl protons, a sharp singlet at δ 4.81 for $S\text{-CH}_2$ protons and a singlet at δ 8.49 for the amide NH protons in addition to signals for other aliphatic and aromatic protons. The ^{13}C NMR spectrum of amide cyclophane **3** showed $S\text{-CH}_2$ carbon at δ 35.9 and amide carbonyl carbon at δ 164.8 in addition to the signals for other aliphatic and aromatic carbons. The mass spectrum (ESI-MS) of **3** showed the molecular ion peak at m/z 696 (M^+). Further, the structure of the amide cyclophane **3** was also confirmed from elemental analysis. Similarly, the structure of the fluorescent amidoanthracenophanes **1** and **4** was confirmed from the spectral and analytical data.

Optical, photophysical, laser and salvatochromism properties of the anthracene bridged fluorescent amidophanes.

The optical and photophysical properties of the anthracene bridged fluorescent amidoanthracenophanes **1**, **2**, **3** and **4** are presented in Table 1. The absorption spectra (1×10^{-5} M) and fluorescence spectra (1×10^{-5} M) of the anthracene bridged fluorescent amidoanthracenophanes **1**, **2**, **3** and **4** in DCM are shown in Fig. 2. The electronic absorption spectra of anthracene bridged fluorescent amidophane **1**, **2**, **3** and **4** shows three intense absorption bands between 373-375, 393-394 and 415-418 nm due to the $\pi\text{-}\pi^*$ transitions of anthracene unit. Anthracene bridged fluorescent amidophane **1**, **2**, **3** and **4** when excited at 370 nm gave three fluorescent emission bands between 401-402, 426-429 and 449-451 nm. All the synthesized fluorescent amidophanes **1**, **2**, **3** and **4** showed the strong fluorescence intensity between 426-429 nm (**Figure 2**), due to the presence of anthracene chromophoric unit in the cyclic system. This confirms that all the cyclophanes have excellent fluorescence property.

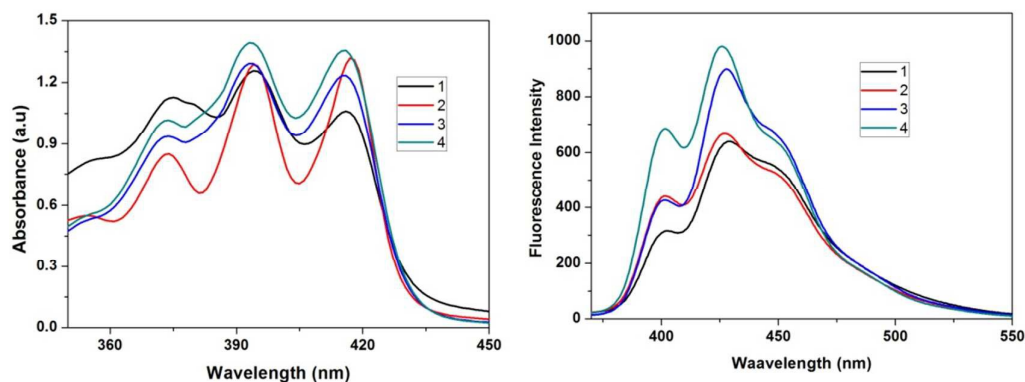


Figure 2. Absorption and emission spectrum of fluorescent amidophanes **1**, **2**, **3** and **4**

Table 1. Optical, photophysical and electrochemical parameters for the fluorescent amidophanes **1**, **2**, **3** and **4** in DCM at 1×10^{-5} M concentration.

Entry No	$\lambda_{\text{abs max}}$ (nm)	$\lambda_{\text{em max}}$ (nm)	Quantum yield (Φ_f)	Life Time (τ) (ns)				Cyclic Voltammetry		
				τ_1	τ_2	τ_3	χ^2	E_{pa}	E_{pc}	
1	375 (113000),									
	394 (126000),	401,	0.29	0.52	2.78	7.13	1.16	-0.49,	-0.77,	
	416 (110000)	426 &								0.57
	449									
2	373 (85000),	402,								
	394 (129000),	427 &	0.21	0.49	2.75	6.40	1.16	-0.51,	-0.75,	
	418 (132000)	450								0.57,
		1.12								1.15
3	374 (94000),	401,								
	393 (129000),	428 &	0.33	0.84	1.49	7.46	1.08	-0.55,	-0.70,	
	416 (123000)	450								0.55
4	373 (102000),	401,								
	393 (139000),	429 &	0.11	0.43	1.93	7.39	1.19	0.28,	-0.42,	
	415 (136000)	451								0.54

Life time decay analysis was carried out with all the fluorescent amidophanes **1**, **2**, **3** and **4** by using Iglesia Bautista Horeb (IBH), Time-Correlated Single Photon Counting

(TCSPC) technique on excitation at 370 nm in DCM as solvent. The fluorescence decay fits as tri-exponential with life time τ_1 , τ_2 and τ_3 . The life time decay of the amidophanes **1**, **2**, **3** and **4** is shown in Table 1. The fluorescence decay (Fig. 3) of amidophanes **1**, **2**, **3** and **4** shows a longer relaxation time τ_2 and τ_3 for the 2nd & 3rd exponential and also shorter relaxation time τ_1 for the 1st exponential.

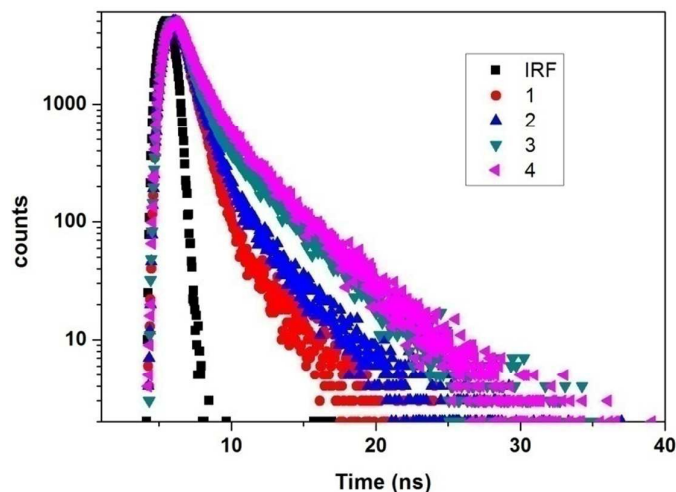


Figure 3. Fluorescence decay of amidophanes **1**, **2**, **3** and **4** (IRF=Instrument Response Function).

The solvatochromism of the synthesized fluorescent amidophanes **1**, **2**, **3** and **4** was carried out by using UV-vis and fluorescence spectroscopy. UV-vis and fluorescence spectra were measured for all the synthesized cyclophanes in five different solvents viz toluene, dichloromethane (DCM), ethyl acetate (EA), acetonitrile (CH₃CN) and tetrahydrofuron (THF) as shown in Fig. 4 for amidophane **1** and as shown in Fig. S1, S2 and S3 (ESI) for amidophanes **2**, **3** and **4**. Summary of the photophysical and electrochemical data of all the compounds are given in Table 2. There is no obvious solvatochromism in the absorption spectra. These four compounds exhibit the rather similar absorption bands in the range of 373–418 nm, which were assigned to the π - π^* transition of the characteristic vibrational structures of the isolated anthracene groups.²⁴ In comparison with the absorption spectra, the

emission spectra are sensitive to the polarity of the solvent as shown in fig 4 for cyclophane 1 in various solvents and the other amidophanes 2, 3 and 4 are shown in ESI (fig S1, fig S2 and fig S3 in). In the presence of various solvents like toluene, ethyl acetate, acetonitrile and THF in absorption and fluorescence spectrum, the peaks are red-shifted and broadened spectra were found compare with DCM for all the compounds. This phenomenon can be explained by the solvent stabilization of the excited state and dipolar interactions between anthracene amidophanes and the polar solvents.²⁶

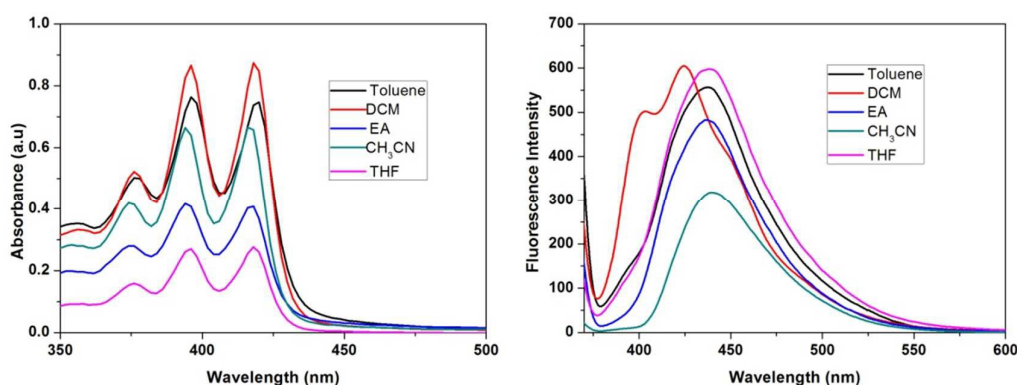


Figure 4. The solvatochromism of the fluorescent amidophane 1 of absorption and emission spectrum.

Electrochemical properties of fluorescent amidophanes 1, 2, 3 and 4

The electrochemical behaviour of the fluorescent amidoanthracenophanes 1, 2, 3 and 4 was studied by cyclic voltammetry with glassy carbon (GC) electrode as working electrode, Pt wire as auxiliary electrode and Ag/AgCl as the reference electrode with 0.1 M TBAP as a supporting electrolyte in dry DCM. The cyclic voltammogram shows the anodic and cathodic peak potential response for all the fluorescent amidoanthracenophanes corresponding to the electrochemical oxidation and reduction process. The fluorescent amidoanthracenophanes 1 shows two oxidation potential at -0.77 and 1.20 as well as two reduction peaks at -0.49 and 0.57. From this study, the synthesized fluorescent amidophanes 1 shows electrochemical property, which can be attributed due to the presence of fluorophoric

anthracene unit. The electrochemical properties are altered due to the presence of aromatic unit such as benzene is present at the intraannular position of the cyclophane. The cyclic voltammogram of the amidocyclophane **2,3** and **4** was shown in SI (Figure S4 and S4a)

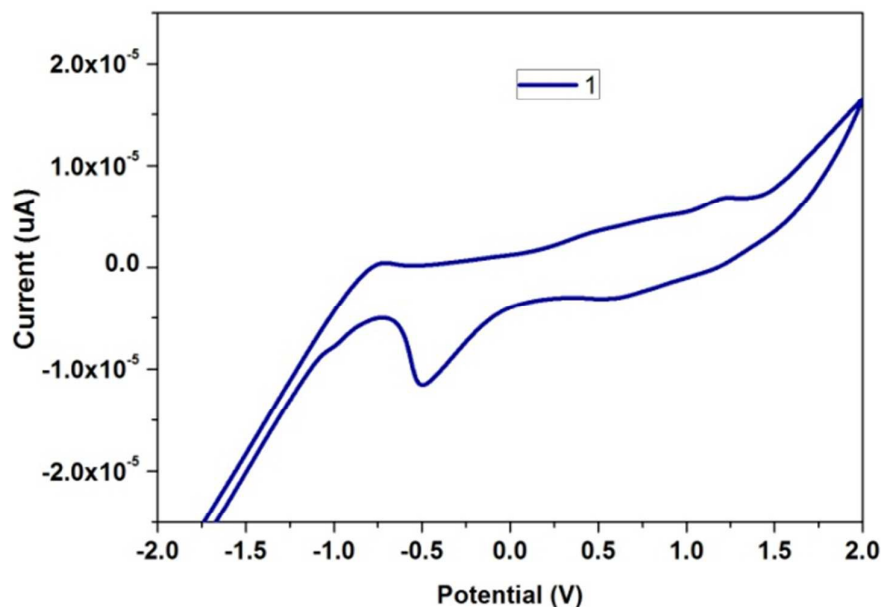


Figure 4. Cyclic voltammograms of fluorescent amidophanes **1** in DCM at room temperature (scan rate at 100 mV s^{-1}) and 0.1 M TBAP as a supporting electrolyte in dry DCM.

Experimental

All reagents were commercially available and used as such unless otherwise stated. Analytical TLC was performed on commercial Merck plates coated with Silica Gel GF254. Analytical samples were obtained by silica gel chromatography, using silica gel of 100-200 mesh and elution with the solvent system as mentioned under each experimental section. The melting points were determined by using a Metler Toledo melting point apparatus by open capillary tube method and were uncorrected. ^1H and ^{13}C NMR spectra were recorded on a 300 MHz BRUKER AVANCE (75 MHz for ^{13}C NMR,) spectrometer. Chemical shifts values are reported in δ ppm relative to internal standard tetramethylsilane (TMS, δ 0.00). ^{13}C chemical shifts (ppm) are reported in δ relative to CDCl_3 (center of triplet,

δ 77.23). The spin multiplicities are indicated by the symbols s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad), dd (doublet of doublets). UV-Vis absorption spectra were measured with a Perkin–Elmer Lambda 35 UV-vis spectrometer, Emissions were recorded on Perkin–Elmer Lambda 45 fluorescence spectrometer and fluorescence quantum yield was determined by exciting the sample at 370 nm with the use of quinine sulfate as the standard ($\Phi_f = 0.546$ in 0.1 N H_2SO_4) recorded on HORIBA JOBIN YVON Fluoromax-4P spectrometer under without N_2 atmosphere. Fluorescence decays were recorded by using an IBH time-correlated single-photon counting spectrometer. The Mass spectra were obtained by EI-MS spectra on JEOL DX-303 mass spectrometer from CLRI, adyar and C, H and N values are obtained Perkin-Elmer 240B elemental analyzer from NCL pune. Cyclic voltammetry measurements were performed in a conventional three electrode system on a CHI model 1100A series electrochemical analyzer (CH Instrument, Austin, TX). The measurements were based on a three electrode system, with a glassy carbon (GC) electrode (of geometric area 0.07 cm^2) being used as the working electrode, a Pt wire in the form of a spiral (with a high geometrical surface area 20 cm^2) being used as the auxiliary electrode and Ag/AgCl as the reference electrode with a scan rate of 100 mV s^{-1} . Tetrabutylammonium perchlorate (TBAP) 0.1 M is used as supporting electrolyte for cyclic voltammetry studies.

Preparation of 9, 10 dichloromethylantracene 5

To a stirred solution of anthracene (1.78 g, 10 mmol), anhydrous ZnCl_2 (1.64 g, 12 mmol), and paraformaldehyde (1.50 g, 50 mmol) in dioxane (20 mL) was slowly added concentrated aqueous hydrochloric acid (1N, 40 mL) at room temperature. After addition, the mixture was refluxed gently for 3 h and allowed to stand for 16 h at room temperature. The resulting fine granular solid was separated by filtration and washed with H_2O and dioxane to afford the crude product. The crude product was recrystallized from toluene to give **5** as

yellowish solid. Yield : 65%, ^1H NMR : (300 MHz, CDCl_3): δ_{H} 5.77 (s, 4H), 7.74-7.77 (m, 4H), 8.53-8.55 (m, 4H). ^{13}C NMR :(75 MHz, CDCl_3): δ_{C} 52.6, 123.5, 125.7, 127.2, 129.4. MS (EI): m/z 275 (M^+).

Synthesis of Precyclophane 7

A mixture of 2-aminobenzenethiol (2.1 equiv.), 9,10-chloromethyl anthracene **7** (1 equiv.), TBAB (5 mg), KOH (2 equiv.), in toluene (20 mL) and water (20 mL) is stirred for overnight at room temperature. Toluene layer was separated, washed with 5% KOH solution (2 x 10 mL) and with water (20 mL). The toluene layer after drying over Na_2SO_4 , was evaporated under vacuum to give the dark yellow colored residue, which was purified by column chromatography using chloroform: hexane (4:1) as eluting solvent to give **7** as pale yellow colour solid. Yield: 86 %, MP : 132-134 °C, ^1H NMR : (300 MHz, CDCl_3): δ_{H} 4.33 (bs, 4H), 4.93 (s, 4H), 6.60-6.69 (m, 2H), 7.00 (d, $J= 8.1$ Hz, 2H), 7.09-7.15 (m, 2H), 7.35 (d, $J= 7.8$ Hz, 2H), 7.45-7.48 (m, 4H), 8.26-8.29 (m, 4H). ^{13}C NMR: (75 MHz, CDCl_3): δ_{C} 32.9, 114.9, 118.3, 118.6, 124.8, 125.6, 129.7, 129.8, 130.8, 136.6, 148.7. MS (EI): m/z 452 (M^+). Elemental Anal. Calcd for $\text{C}_{28}\text{H}_{24}\text{N}_2\text{S}_2$: C, 74.30, H, 5.34, N, 6.19%. Found : C, 74.26, H, 5.31, N, 6.15%.

General procedure for the formation of cyclophanes

2-((10-((2-Aminophenylthio)methyl)anthracen-9-yl)methylthio)benzenamine, **7** (1 equiv., 1.0 mmol) **7** was dissolved in dry CH_2Cl_2 and the solution was cooled to 0 °C. Et_3N (0.61 mL, 4.4 mmol) and then various aromatic dicarboxylic acid chlorides (1.1 equiv., 1.1 mmol) in dry CH_2Cl_2 (30 mL) were added. The mixture was allowed to warm up to room temperature and stirred under nitrogen atmosphere for 15 h. The dark yellow solution was washed with 0.5 M HCl (100 mL) and water (3 x 100 mL) and the organic layer was then collected, dried over Na_2SO_4 and concentrated to dryness. The dark yellow solid residue

obtained was purified by column chromatography using chloroform: methanol as eluting solvent.

Amidoanthracenophanes 1

Amidoanthracenophanes **1** was synthesized as a light yellow solid from 2-((10-((2-Aminophenylthio)methyl)anthracen-9-yl)methylthio)benzenamine (0.5 g, 1.1 mmol) **7** and 1,3-benzenedicarboxylic acid chloride **8** (0.25 g, 1.21 mmol) by using general procedure; Yield : 62%, MP : 165-168 °C, ¹H NMR : (300 MHz, CDCl₃): δ_H 4.82 (s, 4H), 7.18-7.21 (m, 4H), 7.26-7.31 (m, 2H), 7.37-7.42 (m, 2H), 7.44-7.49 (m, 3H), 7.77 (s, 1H), 7.80-7.83(m, 4H), 7.99 (d, *J*=7.5 Hz, 2H), 8.20 (d, *J*= 8.1 Hz, 2H), 8.74 (s, 2H). ¹³C NMR : (75 MHz, CDCl₃): δ_C 35.9, 121.1, 121.9, 124.1, 124.6, 125.1, 125.9, 129.0, 129.3, 130.4, 130.9, 131.1, 135.5, 137.4, 140.7, 164.8. MS (EI): *m/z* 582 (M⁺). Elemental Anal. Calcd for C₃₆H₂₆N₂O₂S₂: C, 74.20, H, 4.50, N, 4.81%. Found: C, 74.16, H, 4.46, N, 4.77%.

Amidoanthracenophanes 2

Amidoanthracenophanes **2** was synthesized as light yellow solid from 2-((10-((2-Aminophenylthio)methyl)anthracen-9-yl)methylthio)benzenamine (0.5 g, 1.1 mmol) **7** and Pyridine dicarboxylic acidchloride **9** (0.247 g, 1.21 mmol) by using general procedure; Yield : 63%, MP : 210-214 °C, ¹H NMR : (300 MHz, CDCl₃): δ_H 4.96(s, 4H), 7.00-7.04 (m, 4H), 7.18 (t, *J*= 9.0 Hz, 2H), 7.23-7.29 (m, 2H), 7.59 (d, *J*= 8.1 Hz, 2H), 7.94 (d, *J*= 7.2 Hz, 2H), 7.98-8.01 (m, 4H), 8.03 (s, 1H), 8.32 (d, *J*= 7.8 Hz, 2H), 9.06 (s, 2H). ¹³C NMR : (75 MHz, CDCl₃): δ_C 34.5, 122.4, 124.4, 125.1, 125.2, 126.1, 127.3, 128.9, 129.8, 130.8, 138.3, 138.6, 140.1, 148.5, 160.9. MS (EI): *m/z* 583 (M⁺). Elemental Anal. Calcd for C₃₅H₂₅N₃O₂S₂: C, 72.02, H, 4.32, N, 7.20%. Found : C, 71.09, H, 4.29, N, 7.15%.

Amidoanthracenophanes 3

Amidoanthracenophanes **3** was synthesized as a light yellow solid from 2-((10-((2-Aminophenylthio)methyl)anthracen-9-yl)methylthio)benzenamine (0.5 g, 1.1 mmol) **7** and 5-n-heptyloxy dicarboxylic acid chloride **10** (0.239 g, 1.21 mmol) by using general procedure; Yield : 62%, MP : 165-167 °C, ^1H NMR : (300 MHz, CDCl_3): δ_{H} 0.90 (t, $J = 5.1$ Hz, 3H), 1.32 (s, 8H), 1.77-1.81 (m, 2H), 3.98 (t, $J = 6.0$ Hz, 2H), 4.81 (s, 4H), 7.19-7.22 (m, 4H), 7.25 (s, 3H), 7.43-7.47 (m, 4H), 7.79-7.82 (m, 4H), 7.98 (d, $J = 7.6$ Hz, 2H), 8.17 (d, $J = 8.4$ Hz, 2H), 8.49 (s, 2H). ^{13}C NMR: (75 MHz, CDCl_3): δ_{C} 14.1, 22.6, 25.9, 29.1, 31.8, 32.9, 35.9, 68.6, 113.7, 116.6, 121.2, 124.2, 124.5, 124.8, 125.9, 129.0, 129.4, 131.0, 137.0, 137.4, 140.7, 159.7, 164.8. MS (EI): m/z 696 (M^+), Elemental Anal. Calcd for $\text{C}_{43}\text{H}_{40}\text{N}_2\text{O}_3\text{S}_2$: C, 74.11, H, 5.79, N, 4.02%. Found : C, 74.06, H, 5.76, N, 3.98%.

Anthraceneamide cyclophane **4**

Amidoanthracenophanes **4** was synthesized as a light yellow solid from 2-((10-((2-Aminophenylthio)methyl)anthracen-9-yl)methylthio)benzenamine (0.5 g, 1.1 mmol) **7** and thiophene 2,5-dicarboxylic acid chloride **11** (0.25 g, 1.21 mmol) by using general procedure; Yield : 64%, MP : 198-203 °C, ^1H NMR : (300 MHz, CDCl_3): δ_{H} 5.00 (s, 4H), 7.31 (d, $J = 7.5$ Hz, 2H), 7.40-7.43 (m, 4H), 7.53 (t, $J = 7.5$ Hz, 2H), 7.60 (s, 2H), 7.96 (d, $J = 7.8$ Hz, 2H), 7.99-8.02 (m, 4H), 8.42 (d, $J = 8.1$ Hz, 2H), 8.69 (s, 2H). ^{13}C NMR : (75 MHz, CDCl_3): δ_{C} 36.5, 120.4, 124.6, 124.8, 125.1, 126.5, 129.2, 131.1, 132.2, 132.6, 137.0, 139.4, 140.2, 158.7. MS (EI): m/z 588 (M^+), Elemental Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_2\text{S}_3$: C, 69.36, H, 4.11, N, 4.76%. Found: C, 69.31, H, 4.07, N, 4.71%.

Fluorescence measurement

The photoluminescence (PL) spectra of the synthesized fluorescent amidoanthracenophanes **1**, **2**, **3** and **4** are recorded under without N_2 atmosphere in 1×10^{-5} M concentration in DCM and excited at 370 nm.

Conclusion

In conclusion, all the fluorescent amidophanes **1**, **2**, **3** and **4** were successfully synthesized in excellent yield. All the amidophanes are fluorescent in nature and the optical, photophysical and electrochemical properties are altered due to the presence of various aromatic units at the intraannular position of the cyclophane. All the amidophanes emit blue light under ultra violet irradiation, such property is very useful for chemical sensors and for exhibiting OLED properties. The sensing ability of such amidophanes against various metal cations, anions and also biomolecules like DNA is underway.⁰

Supporting Information

The detailed spectrum of optical and fluorescence of the synthesized amidophanes **2**, **3** and **4** and also optical and photophysical parameters. The ¹H NMR and ¹³C NMR details are present in the electronic supporting information (ESI).

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