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Synthesis, characterization, photophysical and electrochemical properties of triazinooxacalix[2]arenes with bisphenol A motif

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ABSTRACT

Oxygen atom bridged calixarene derivatives called oxacalixarenes were synthesized from bisphenol A and cyanuric chloride by aromatic nucleophilic substitution through addition elimination mechanism. All the synthesized oxacalixarenes exhibit strong absorbance band between 225 and 286 nm due to the presence of triazine and phenoxy units. The oxacalixarenes **7** and **10** show strong fluorescence emission and higher λ_{em} values than all other oxacalixarenes due to the presence of rigid aromatic spacer units such as binol and biphenyl. All the oxacalixarenes exhibit quasi-reversible behaviour and potential shift observed in cyclic voltammetry.

1. Introduction

The design and synthesis of new and functional macrocyclic host molecules has been one of the driving forces to promote the major advances in supramolecular chemistry.[1] Crown ether type of calixarenes are the third generation of supramolecules,[2] which consists of the upper rim and a narrow lower rim and a central annulus. Calix[n]arene are [1_n] metacyclophane which are relatively easy to prepare and functionalize due to their high level preorganization and conformational preferences. Calixarenes are useful host molecules in supramolecular systems and have a wide range of industrial applications such as metal sequestration and waste remediation.[3] Incorporation of the bridging atoms other than carbon within 'classical' carbon-bridged calix[n]arenes framework provide means to produce new macrocyclic host molecules called heterocalixarenes with unexplored chemical and physical properties.[4] Recently, Katz and co-workers[5] reported a new class of oxacalixarenes based on molecular tweezers which shows the capability of binding aromatic guest molecule.

The chemistry of heterocalixarene[6] has a growing interest in calixarene field because of the easy availability, fine tunable cavities and potential applications in supramolecular chemistry. The calixarene skeleton can be modified with heteroatoms including sulfur[7] and nitrogen[8] along with the bridging oxygen.[9] Heteroeocalixarenes can be synthesized either by fragment coupling approach[10] or by one pot macrocyclic condensation.[11] The electronic properties and the cavity size can be tuned in calixarenes to improve their self-assembly and recognition abilities. The heterocalixarene play an important role in host-guest chemistry[12] with various guest species like cations, anions and neutral molecules including fullerenes. Oxacalixarene[13] is an important class of the heterocalixarenes that has shown a fast growth in the calixarene chemistry due to increasing amount of effort devoted to the synthesis and conformational investigation. The oxacalixarene derivatives have been reported earlier for the detection of explosives due to their ability to form host-guest complexes through specific chemical interactions.[14] The heterocalixarenes containing triazine bridge with either oxygen or nitrogen bridging atom could have different degree of conjugation with the neighbouring aromatic rings. Such macrocycles have definite electronic characteristics, unique binding properties and to complex with acidic guest molecules.[15] Electron deficient triazine rings in the oxacalixarene forms ternary complexes with halide ion and possess water molecule in the solid state.[16] Such complexes could have anion-π interaction between the halide ion and one triazine ring.

Melamine is one of the triazine derivatives widely used as building block in supramolecular chemistry, generating a wide range of the structural motifs, including cyclic rosettes,[17] linear or crinkled tapes[18] and molecular strands or ribbons.[19] Oxacalixarenes can exist in thermodynamically favourable 1,3 alternate (partial

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cone) arrangement and explore their broad applications such as ion sensitive electrodes,[20] sensors,[21] self-assembly[22] and for the measurement of sodium levels in blood.[23] The oxacalixarenes can be synthesized by aromatic nucleophilic substitution reaction through addition and elimination mechanism of the bisphenol A with cyanuric chloride by step wise fragment coupling approach. The present investigation deals with synthesis, structural characterization and optical as well as electrochemical properties of the oxacalixarenes **1**–**10** (Fig. 1) with bisphenol A at the intra annular position.

2. Results and discussion

The oxacalixarenes **1**–**10** can be synthesized by aromatic nucleophilic substitution[24] through addition elimination mechanism. The precycophane **13** was obtained in **87%** by the reaction of 1.0 equiv. of the bisphenol A **11** with 2.1 equiv. of cyanuric chloride **12** in the presence of DIPEA in dry THF (Scheme 1). To avoid the formation of bis and tris alkylated product, ice bath was used and the yield of **13** can be slightly improved when a large excess amount of cyanuric chloride **12** was used. Under optimized conditions the yield of the precyclophane **13** obtained was only **40%.** When THF was used as the solvent with different bases such as Et_3N and K_2CO_3 instead of DIPEA, the yield of the precyclophane **13** was reduced drastically. In the ^{1}H NMR spectrum, the precyclophane **13** displayed a six proton singlet at δ 1.74 for two methyl group attached to the bisphenol A unit and a two proton doublet at δ 7.11 and a two proton doublet at δ 7.33 for the protons in the benzene ring of the bisphenol A unit. In the ^{13}C NMR spectrum the precyclophane **13** showed the methyl carbon of the bisphenol A unit at δ 30.9 in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (HRMS) of the precyclophane **13** showed molecular ion peak at *m/z* 525.1869 $[M + H]^+$ along with isotopic peaks at 527.1678 and 529.1403. Further, the structure of the precyclophane **13** was also confirmed from the spectral and analytical data.

With the precyclophane **13** in our hand, the synthesis of the oxacalixarenes **1** to **10** was then focused under various reaction conditions. To optimize the yield of the oxacalixarenes **1**–**10**, various solvents such as acetone, THF and acetonitrile were employed for the reaction of the precyclophane **13** with the bisphenol A **11**. The use of acetonitrile or THF for the macrocyclic coupling gave only **24%** yield of the oxacalixarene **1**. However the yield of oxacalixarene **1** was better **(36%)** in acetone than in any other solvents. To improve the yield of the oxacalixarene **1**, the reaction of the precyclophane **13** with the bisphenol A **11** was tried using various inorganic and organic bases such as K_2CO_3, Na_2CO_3 and Et_3N, but still the yield of **1** was poor (**10%).** However macrocyclic coupling of 1.0 equiv. of the bisphenol A **11** with 1.0 equiv. of the precyclophane **13** in the presence of DIPEA in acetone under high dilution conditions at room temperature for 48 h gave the oxacalixarene **1** in **36%** yield (Scheme 1).

The high dilution technique has been employed to avoid the formation of linear trimeric and polymeric products and also the higher order oligomers such as 3:3 and 4:4. However all such higher order oligomers are insoluble and hence chromatographic technique could not be employed for the purification of such polymeric and higher order oligomeric products. In the ^{1}H NMR spectrum, the oxacalixarene **1** showed a twelve proton singlet at δ 1.67 for the methyl protons of the bisphenol A unit in addition to the signals for the aromatic protons. In the ^{13}C NMR spectrum, the

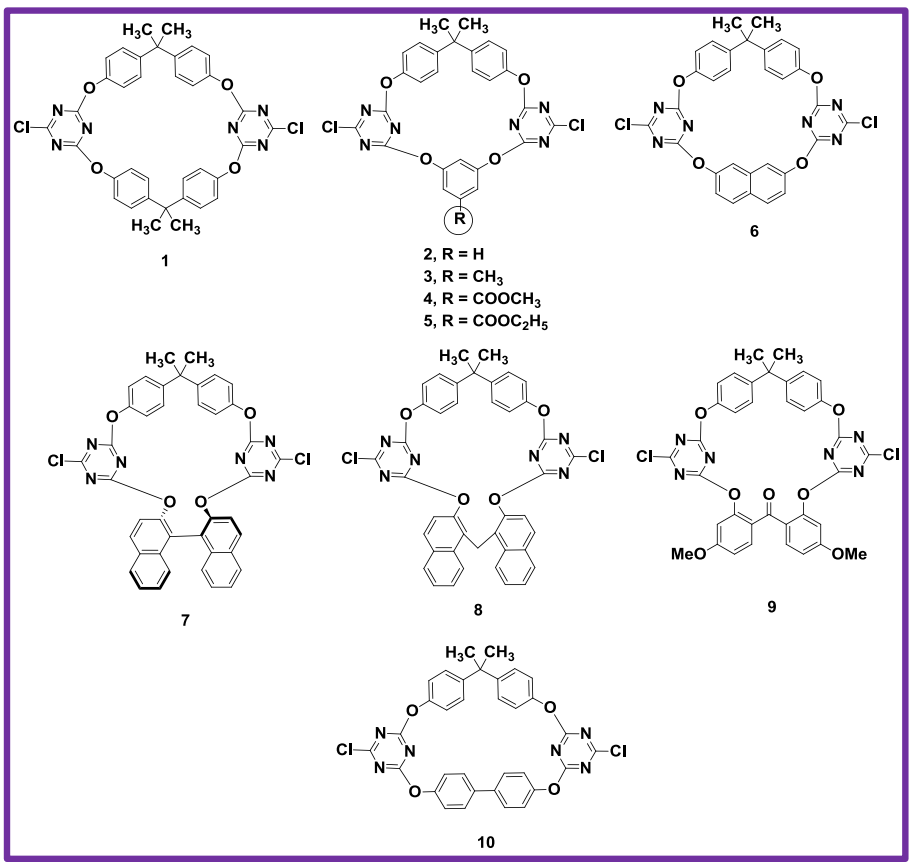

Fig. 1. Molecular structure of the oxacalixarenes **1**–**10** with bisphenol A unit at intra annular position.

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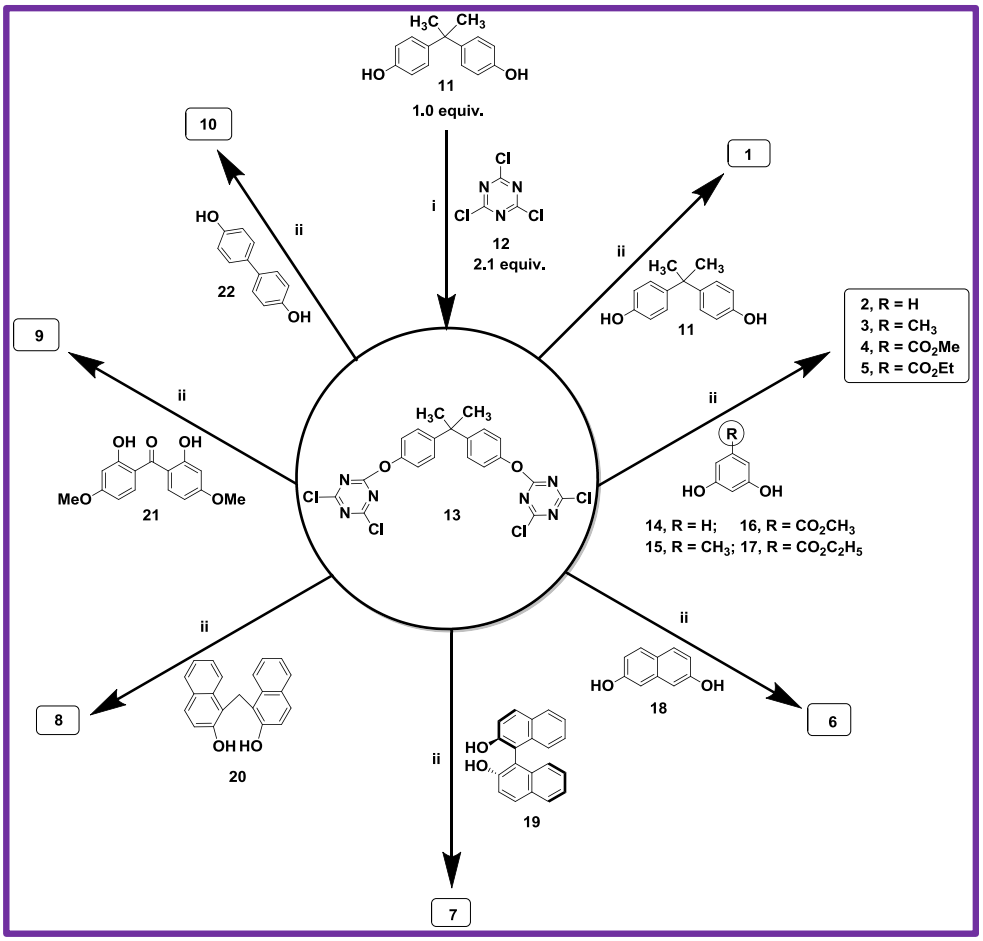

Scheme 1. (i) DIPEA, dry THF, 0 °C to rt, 4 h (ii) DIPEA, acetone, rt, 48 h.

oxacalixarene **1** displayed the methyl carbon attached to the bisphenol A at δ 68.9, in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (HRMS) of the oxacalixarene **1** showed molecular ion peak at *m/z* 679.1611 $[M + H]^+$ along with the isotopic peaks at 681.1519 and 682.1503 (SI, Fig. S4.1). Further, the structure of the oxacalixarene **1** was also confirmed from elemental analysis.

Similarly, the oxacalixarenes **2**, **3, 4** and **5** were obtained in **28%, 22%, 20%** and **21%** yields, respectively by the reaction of the resorcinol derivatives **14**, **15, 16** and **17** with the precyclophane **13** for 48 h in acetone in the presence of DIPEA at room temperature under high dilution condition. In the ^{1}H NMR spectrum, the oxacalixarene **4** showed six proton singlet at δ 1.73 for the methyl attached to the bisphenol A unit and the three proton singlet at δ 4.05 for the ester methoxy protons in addition to the signals for the aromatic protons. In the ^{13}C NMR spectrum, the oxacalixarene **4** displayed the methyl carbons attached to the bisphenol A unit at δ 28.7 and the ester methoxy carbon at δ 52.7, in addition to the other aliphatic and aromatic carbon signals. The mass spectrum (HRMS) of the oxacalixarene **4** showed the molecular ion peak at *m/z* 619.0908 $[M + H]^+$ along with the isotopic peaks at 621.0880 and 623.0564 (SI, Fig. S4.3).

The oxacalixarene **8** was obtained in **28%** yield by the macrocyclization of the precyclophane **13** under high dilution condition with methylene binaphthol **20** for 48 h in acetone in the presence of DIPEA at room temperature. The ^{1}H NMR spectrum of the oxacalixarene **8** displayed a six proton singlet at δ 1.73 for the two methyl attached to bisphenol A unit and two proton singlet at δ 4.95 for methylene protons located in between the two naphthyl rings in addition to the signals for the aromatic protons. In the ^{13}C NMR spectrum the oxacalixarene **8** showed the methylene carbon in between the two naphthyl rings and the methyl carbon in bisphenol A at δ 24.0, 28.8 respectively, in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (HRMS) of the oxacalixarene **8** showed the molecular ion peak at *m/z* 751.1656 $[M + H]^+$ in addition to the isotopic signals at 753.1761 and 755.1962 (SI, Fig. S4.4). Further, the structure of the oxacalixarene **8** was also confirmed from elemental analysis. Similarly, the reaction of the 4,4′-dimethoxy-2,2′-dihydroxybenzophenone **21** with the precyclophane **13** in the presence of DIPEA in for 48 h acetone under high dilution conditions at room temperature gave the oxacalixarene **9** in **20%** yield. In the ^{1}H NMR spectrum, the oxacalixarene **9** showed a singlet at δ 1.59 for the two methyl attached to bisphenol A unit and a six proton singlet at δ 3.81 for methoxy protons in addition to the signals for the aromatic protons. In the ^{13}C NMR spectrum, the oxacalixarene **9** displayed the bisphenol A attached to methyl carbon and the ester methoxy carbon at δ 28.8, 55.8, respectively, in addition to the signals for the other aliphatic and aromatic carbons. The mass spectrum (HRMS) of the oxacalixarene **9** showed the molecular ion peak at *m/z* 725.1310 $[M + H]^+$ along with isotopic peak at 727.1447 and 728.1532 (SI, Fig. S4.5). Further, the structure of the oxacalixarene **9** was confirmed from elemental analysis. Finally, in order to create structural rigidity the biphenyl-4,4′-diol **22** was reacted with the precyclophane **13** to give the oxacalixarene **10** in **22%** yield. The structure of the oxacalixarenes **2**, **3**, **5**, **6**, **7** and **10** was also

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confirmed from spectral and analytical data.

The oxacalixarenes **1**–**10** has two chlorine atoms on the upper rim and hence further functionalization could be carried out using 2.1 equiv. of the various nucleophiles such as amines and pyridine through addition elimination mechanism. Such transformation has been reported in the literature,[25] however the reaction of the oxacalixarenes **1** to **10** with various amines gave only mixture of the inseparable products and various techniques to purify the products was futile and hence the structure of the products could not be identified.

3. Photophysical properties

The UV–vis absorption spectra of the oxacalixarenes **1**–**10** were recorded in CH_3CN (1×10^{-3} L mol^{-1} cm^{-1}) and the λ_{max} values are summarized in Table 1. The UV–vis spectrum of the oxacalixarenes **1**–**10** exhibit strong absorption band between 225 and 286 nm which shows π-π^* transition due to the presence of triazine and phenoxy units in the cyclic systems as shown in Fig. 2(a and b).

The molar absorptivity for the oxacalixarenes **3** and **5** is found to be high due to the presence of electron donating and electron withdrawing group in the intra annular position, which indicate that the oxacalixarenes **3** and **5** show self-complementary property. The molar absorptivity of the oxacalixarenes **7** and **9** is found to be low due to the presence of rigid binol system and electron withdrawing benzophenone chromopore as the spacer units. However the oxacalixarene **8** shows a small hypsochromic or blue shift when compared with other than oxacalixarenes due to presence of the methylene unit in between the two naphthyl ring system which could prevent the conjugation.

Fluorescence emission spectrum was obtained by exciting all the oxacalixarenes **1**–**10** at the corresponding absorption maximum.

Table 1
Photophysical properties of the oxacalixarenes **1**–**10** in acetonitrile.

Oxacalixarenes	λ_{max} (nm)	ε (L·mol^{-1}·cm^{-1})	λ_{em} (nm)
1	231	690	431
2	227	710	428
3	227, 279, 286	1000, 260, 220	431
4	229	660	432
5	226, 279, 285	1190, 230, 230	433
6	249	700	432
7	228	560	435
8	225	880	432
9	282	620	430
10	249	950	434

The oxacalixarenes **1**–**10** show a strong emission band in the range of 428–435 nm as shown in Fig. 3(a and b) and Table 1. The oxacalixarenes **7** and **10** show a strong fluorescence emission with higher λ_{em} values when compared with other than oxacalixarenes due to the presence of highly π-conjugated aromatic chromophores such as binol and biphenyl units, respectively. Similarly, fluorescence intensity of the oxacalixarenes **2** and **9** shows weak emission due to presence of the electron donating substituent in the spacer units.

4. Electrochemical studies

The redox property of oxacalixarenes **1**–**10** was studied using the cyclic voltammetry. The cyclic voltammogram of the oxacalixarenes **1**–**10** was obtained in acetonitrile containing 0.1 M TBAP as the supporting electrolyte at scan rate is 100 mV s^{-1} as shown in Fig. 4 and Table 2. The oxacalixarenes **1, 2** and **3** exhibited two oxidation peaks between −0.30–1.67 V and two reduction peaks between 1.18 and −1.43 V and the oxacalixarenes **4, 5, 6, 9** and **10** showed two oxidation signal and one reduction signal due to presence of the electron donating substituents in the molecular systems. But the oxacalixarenes **7** and **8** exhibit three oxidation and three reduction peaks due to extended π-conjugated binol and methylene binaphthol spacer units in the molecular frame. All the oxacalixarenes exhibit the oxidation reduction signals with quasi-reversible behaviour in cyclic voltammetry.[26]

The reversible oxidation potential of oxacalixarene **1** with the positive potential value of 1.64 V is due to presence of the electron rich phenoxy group and electron deficient triazine rings. For the oxacalixarenes **2** and **3**, the oxidation potential value gradually increases due to electron donating groups. However, for the oxacalixarenes **4** and **5**, the potential value gradually decreases and the potential shift was observed at 1.67 and 1.54 V respectively due to the presence of electron withdrawing carbethoxy group. The oxacalixarenes **6** and **7** with extensive π-conjugation with the triazine moiety exhibit less shift in the oxidation potential at 0.47 and 0.48 V respectively due to presence of the aromatic spacer units viz: naphthalene and binol.

The oxacalixarene derivatives **8**, **9** and **10** have higher positive potential in the order is 1.17, 1.05 and 1.44 V respectively due to highly conjugated delocalized π-electrons and electron deficient triazine rings. The cathodic peak potential for the oxacalixarenes **1**–**10** shows a higher negative potential range at −0.02 to −1.22 V is due to structural rigidity of the aromatic spacer units. However, oxacalixarene derivatives **6**, **7**, **8**, **9** and **10** with extensive π-conjugation with triazine rings require more energy for the

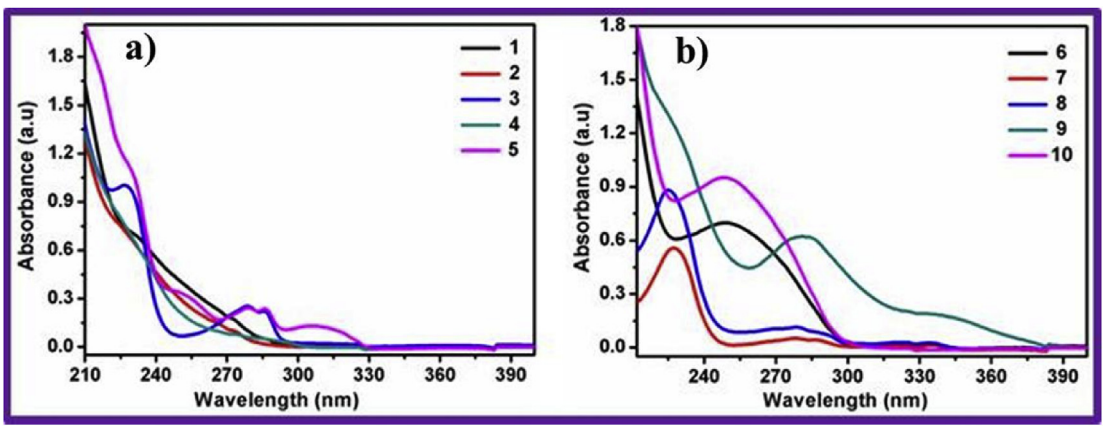

Fig. 2. UV–vis absorption spectra of **a)** the oxacalixarenes **1**–**5** and **b)** the oxacalixarenes **6**–**10** in acetonitrile.

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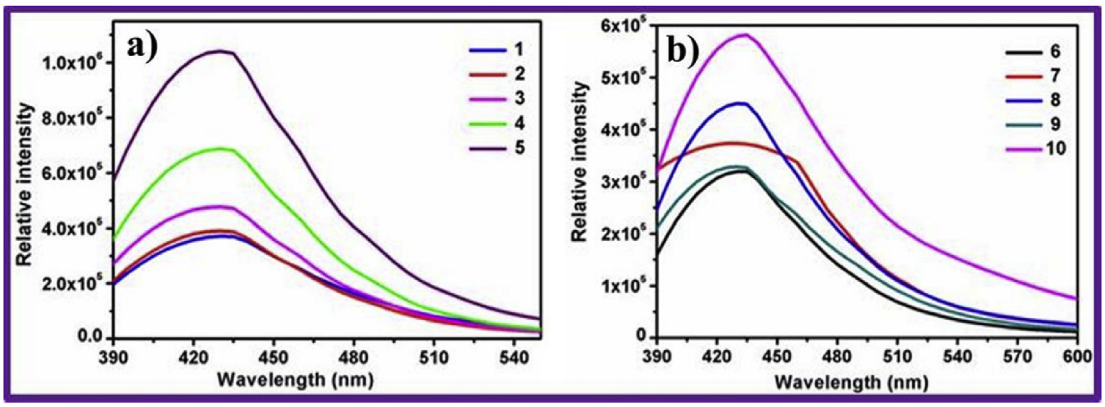

Fig. 3. Emission spectra of a) the oxacalixarenes **1**–**5** and the oxacalixarenes **6**–**10** in acetonitrile.

reduction process[27] and the negative potential shift was observed from the lower to higher potential value in the cyclic voltammetry.

5. Experimental section

5.1. Material and methods

All the reagents and solvents were obtained from Alfa Aesar, Merck or Avra chemical companies. The known products were identified by the comparison of their melting points and spectral data is already reported in the literature. Melting points were uncorrected and were determined using Toshniwal melting point apparatus by the open capillary tube method. The UV–Vis spectra were recorded on a Hitachi U-3210 spectrophotometer. The emission spectra were recorded on a HORIBA JOBIN YVON Fluoromax-4 spectrophotometer. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. The chemical shifts are reported in ppm (δ) with TMS as an internal standard and the coupling constants (J) are expressed in Hz. High resolution mass spectra (HRMS) were recorded on Q-Tof Micro mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240B elemental analyser. Electrochemical studies were carried out on a CH Instrument electrochemical analyser.

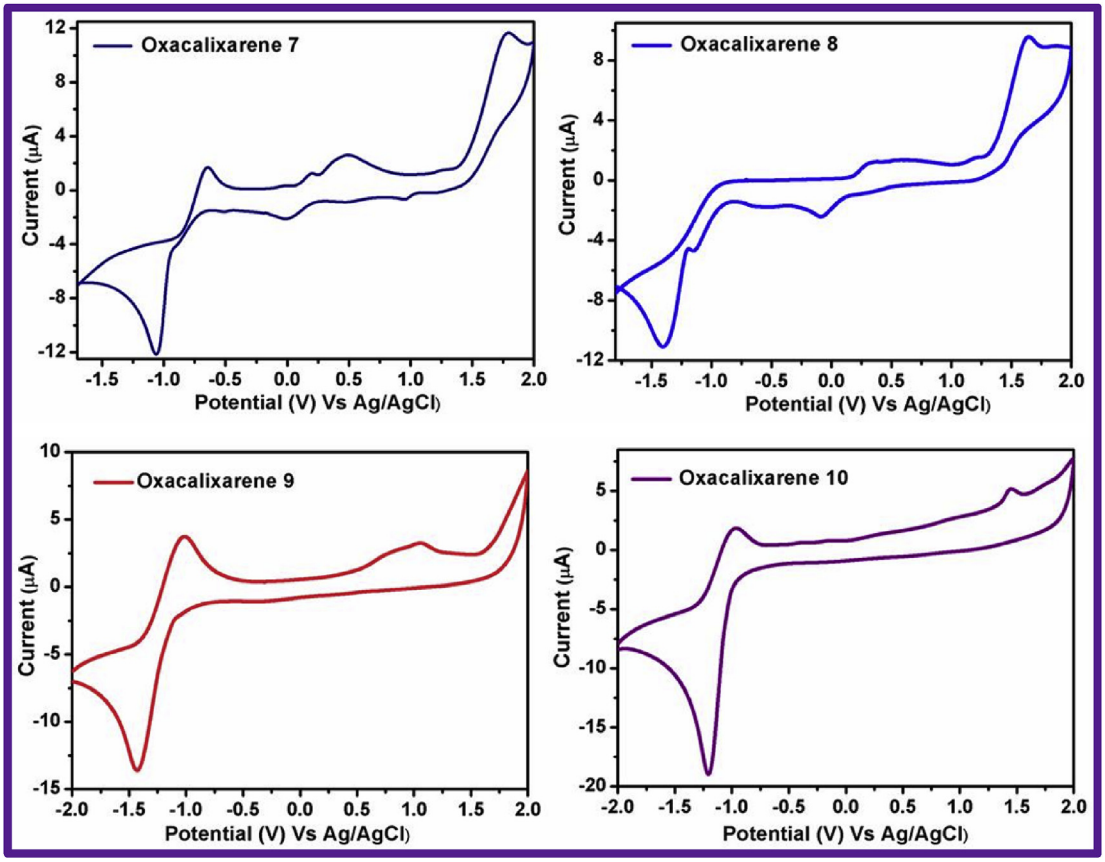

Fig. 4. Cyclic voltammogram of the oxacalixarenes **7**–**10** in acetonitrile scanned at 100 mV s^{-1}.

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Table 2
Electrochemical parameters of the oxacalixarenes **1**–**10** in acetonitrile.

compd	$E_{pc}1$ (V)	$E_{pc}2$ (V)	$E_{pc}3$ (V)	$E_{pa}1$ (V)	$E_{pa}2$ (V)	$E_{pa}3$ (V)	ΔEp1(V)	ΔEp2 (V)	ΔEp3 (V)
1	−0.52	1.64	-	1.17	−1.15	–	−1.69	2.79	-
2	−0.54	1.61	-	1.16	−1.14	–	−1.70	2.75	-
3	−0.44	1.68	–	1.18	−1.19	–	−1.62	2.87	–
4	1.41	1.67	–	−1.22	–	–	0.19	1.67	–
5	1.07	1.54	–	−0.49	–	–	1.56	1.54	–
6	−0.30	0.47	-	−0.75	–	–	0.45	0.47	-
7	−0.64	0.48	1.78	0.96	−0.02	−1.05	−1.60	0.50	2.83
8	0.32	1.17	1.63	−0.07	−1.13	−1.40	0.44	2.43	3.03
9	−1.01	1.05	-	−1.43	–	–	0.42	1.05	-
10	−0.97	1.44	-	−1.21	–	–	0.24	1.44	-

5.2. Synthesis of precyclophane 13

To a solution of DIPEA/(4.0 equiv.) in dry THF (200 mL) in ice bath, Bisphenol A (2 g, 14 mmol) and cyanuric chloride (6.10 g, 33 mmol) each in dry THF (100 mL) was separately and simultaneously added in dropwise under high dilution condition during a period of 4 h. The reaction mixture was stirred for another 4 h at room temperature. After the reaction was complete, the solvent was removed under reduced pressure and then extracted with EtOAc (3 × 100 mL). The combined organic layer was washed with water (100 mL) and brine (50 mL) and dried over anhydrous Na_2SO_4. Ethyl acetate was removed under reduced pressure and the final residue was purified by column chromatography on silica gel using n-Hexane:EtOAc (9:1) as the eluent to afford the pure precyclophane **13** as colourless solid (3.0 g, 87%); mp: 242–244 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.74 (s, 6H); 7.11 (d, J = 8.1 Hz, 4H); 7.33 (t, J = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 30.9, 42.7, 120.4, 128.3, 148.8, 149.0, 171.0, 173.0. HRMS (EIS-MS) m/z 525.1869 [M + H]$^+$.

5.3. General procedure for the synthesis of oxacalixarenes (procedure A)

To a solution of DIPEA (4.78 mmol, 2.5 equiv.) in acetone (200 mL), precyclophane (1.91 mmol, 1.0 equiv.) and dihydroxy derivatives (1.91 mmol, 1.0 equiv.) each in acetone (100 mL) was separately and simultaneously added in dropwise under high dilution condition during a period of 4 h. The reaction mixture was further stirred for another 48 h at room temperature. The solvent was then removed under reduced pressure and washed with water (50 mL) to give the residue which was then extracted with EtOAc (3 × 100 mL). The combined organic phase was washed with water (50 mL), brine (50 mL) and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure to give a residue, which was purified by column chromatography on silica gel using the eluent as mentioned under each compound.

5.3.1. Oxacalixarene 1

Following the general procedure **A**, oxacalixarene **1** was obtained as colourless solid from precyclophane **13** (0.5 g, 0.96 mmol) and bisphenol A **11** (0.24 g, 1.05 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 36%; mp: 270–272 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.67 (s, 12H); 7.02 (d, J = 8.1 Hz, 8 H); 7.11 (d, J = 8.1 Hz, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 31.4, 42.9, 120.9, 127.5, 148.4, 149.3, 171.6, 173.9. HRMS (EIS-MS) m/z 679.1611 [M + H]$^+$. Anal. Calcl. for $C_{36}H_{28}Cl_2N_6O_4$: C, 63.63; H, 4.15; N, 12.37. Found: C, 63.85; H, 4.39; N, 12.06%.

5.3.2. Oxacalixarene 2

Following the general procedure **A**, oxacalixarene **2** was obtained as colourless solid from precyclophane **13** (1.0 g, 1.91 mmol) and resorcinol **14** (0.22 g, 2.00 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 28%; mp: 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.74 (s, 6H); 6.88 (d, J = 8.4 Hz, 3 H); 6.99 (d, J = 8.4 Hz, 4H); 7.17 (d, J = 8.4 Hz, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 29.0, 41.6, 112.7, 118.1, 120.5, 126.9, 148.1, 148.6, 151.4, 171.0, 171.9, 174.5. HRMS (EIS-MS) m/z 561.0843 [M + H]$^+$. Anal. Calcl. for $C_{27}H_{18}Cl_2N_6O_4$: C, 57.77; H, 3.23; N, 14.97. Found: C, 57.49; H, 3.49; N, 14.66%.

5.3.3. Oxacalixarene 3

Following the general procedure **A**, oxacalixarene **3** was obtained as colourless solid from precyclophane **13** (0.5 g, 0.95 mmol) and 3,5-dihydroxytoluene **15** (0.15 g, 1.05 mmol) and after eluting the from column with EtOAc:Hexane (1:4). Yield: 22%; mp: 248–250 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.76 (s, 6H); 2.28 (s, 3H); 6.66 (s, 1H); 6.70 (s, 2H); 7.01 (d, J = 8.7 Hz, 4H); 7.22 (d, J = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 21.5, 28.9, 41.5, 109.6, 118.7, 120.6, 126.7, 138.3, 148.0, 148.7, 151.0, 171.0, 171.9, 174.4. HRMS (EIS-MS) m/z 575.4022 [M + H]$^+$. Anal. Calcl. for $C_{28}H_{20}Cl_2N_6O_4$: C, 58.45; H, 3.50; N, 14.61. Found: C, 58.18; H, 3.72; N, 14.26%.

5.3.4. Oxacalixarene 4

Following the general procedure **A**, oxacalixarene **4** was obtained as colourless solid from precyclophane **13** (1.0 g, 1.91 mmol) and 3,5-dihydroxymethylbenzoate **16** (0.34 g, 2.01 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 20%; mp: 230–232 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.73 (s, 6H); 4.05 (s, 3H); 7.01 (d, J = 8.1 Hz, 5H); 7.16 (d, J = 7.5 Hz, 4H); 7.61 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 28.7, 41.4, 52.7, 116.9, 119.6, 120.7, 126.6, 130.3, 147.9, 148.6, 151.1, 170.8, 172.0, 174.8. HRMS (EIS-MS) m/z 619.0908 [M + H]$^+$. Anal. Calcl. for $C_{29}H_{20}Cl_2N_6O_6$: C, 56.23; H, 3.25; N, 13.57. Found: C, 55.95; H, 3.44; N, 13.27%.

5.3.5. Oxacalixarene 5

Following the general procedure **A**, oxacalixarene **5** was obtained as colourless solid from precyclophane **13** (0.58 g, 0.95 mmol) and 3,5-dihydroxyethylbenzoate **17** (0.18 g, 1.01 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 21%; mp: 238–240 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.50 (t, J = 7.2 Hz, 3H); 1.73 (s, 6 H); 4.50 (q, 2H); 7.02 (d, J = 8.7 Hz, 5H); 7.15 (d, J = 8.7 Hz, 4H); 7.61 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 14.5, 28.7, 41.4, 61.9, 116.6, 119.5, 120.7, 126.6, 130.7, 147.9, 148.6, 151.1, 164.3, 170.8, 171.9, 174.9. HRMS (EIS-MS) m/z 633.4383 [M + H]$^+$. Anal. Calcl. for $C_{30}H_{22}Cl_2N_6O_6$: C, 56.88; H, 3.50; N, 13.27. Found: C, 56.65, H, 3.68; N, 12.94%.

5.3.6. Oxacalixarene 6

Following the general procedure **A**, oxacalixarene **6** was obtained as colourless solid from precyclophane **13** (0.8 g, 1.53 mmol) and naphthalene-2,7-diol **18** (0.25 g, 1.53 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 25%; mp:

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218–220 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.56 (s, 6H); 6.95 (d, J = 7.8 Hz, 3H); 7.09 (d, J = 7.5 Hz, 4H); 7.16 (d, J = 7.5 Hz, 4H); 7.53 (d, J = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 32.5, 43.3, 120.4, 122.2, 127.4, 127.6, 138.0, 147.6, 149.9, 151.3, 171.4, 172.7, 174.2. HRMS (EIS-MS) m/z 611.4343 $[M + H]^+$. Anal. Calcl. for $C_{31}H_{20}Cl_2N_6O_4$: C, 60.89; H, 3.30; N, 13.74. Found: C, 60.65; H, 3.62; N, 13.46%.

5.3.7. Oxacalixarene 7

Following the general procedure **A**, oxacalixarene **7** was obtained as colourless solid from precyclophane **13** (0.8 g, 1.53 mmol) and (*S*)-Binol **19** (0.46 g, 1.60 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 24%; mp: 286–288 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.77 (s, 6H); 6.56 (d, J = 7.5 Hz, 4 H); 7.05 (d, J = 7.5 Hz, 4H); 7.24 (d, J = 9.3 Hz, 4H); 7.46 (d, J = 8.4 Hz, 4H); 7.94 (t, J = 8.4 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 28.6, 41.8, 120.3, 120.7, 122.2, 125.9, 126.2, 126.6, 127.1, 128.0, 129.0, 131.5, 132.9, 146.8, 148.5, 149.0, 171.0, 172.6, 173.5. HRMS (EIS-MS) m/z 737.5889 $[M + H]^+$. Anal. Calcl. for $C_{41}H_{26}Cl_2N_6O_4$: C, 66.76; H, 3.59; N, 16.61. Found: C, 66.49; H, 3.79; N, 16.32%.

5.3.8. Oxacalixarene 8

Following the general procedure **A**, oxacalixarene **8** was obtained as violet solid from precyclophane **13** (0.35 g, 0.66 mmol) and methylenebinaphthol **20** (0.20 g, 0.66 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 28%; mp: 194–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.73 (s, 6H); 4.95 (s, 2H); 6.63 (d, J = 7.8 Hz, 4H); 6.98 (d, J = 6.9 Hz, 6H); 7.39 (d, J = 7.5 Hz, 2H); 7.47 (m, 4H); 7.81 (d, J = 7.5 Hz, 2H); 8.13 (d, J = 8.1 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ_C 24.0, 28.8, 42.0, 120.1, 120.5, 124.4, 125.4, 125.7, 126.3, 127.2, 127.7, 128.5, 131.8, 132.8, 147.1, 148.7, 149.0, 170.8, 172.4, 173.4. HRMS (EIS-MS) m/z 751.1656 $[M + H]^+$. Anal. Calcl. for $C_{42}H_{28}Cl_2N_6O_4$: C, 67.12; H, 3.75; N, 11.80. Found: C, 66.89; H, 3.91; N, 11.57%.

5.3.9. Oxacalixarene 9

Following the general procedure **A**, oxacalixarene **9** was obtained as colourless solid from precyclophane **13** (1.0 g, 1.91 mmol) and 4,4′-Dimethoxy-2,2′-dihydroxybenzophenone **21** (0.55 g, 2.01 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 20%; mp: 290–292 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.59 (s, 6H); 3.81 (s, 6H); 6.60 (m, 4H); 6.90 (d, J = 8.4 Hz, 4H); 7.13 (t, J = 8.4 Hz, 2H); 7.16 (s, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ_C 28.8, 41.9, 55.8, 107.1, 117.7, 120.6, 124.4, 127.4, 132.4, 148.5, 149.4, 151.1, 163.0, 171.5, 172.6, 173.9, 189.5. HRMS (EIS-MS) m/z 725.1310 $[M + H]^+$. Anal. Calcl. for $C_{36}H_{26}Cl_2N_6O_7$: C, 59.60; H, 3.61; N, 11.58. Found: C, 59.39; H, 3.79; N, 11.30%.

5.3.10. Oxacalixarene 10

Following the general procedure A, oxacalixarene **10** was obtained as colourless solid from precyclophane **13** (0.8 g, 1.53 mmol) and biphenyl-4,4′-diol **22** (0.29 g, 1.59 mmol) and after eluting from the column with EtOAc:Hexane (1:4). Yield: 22%; mp: 258–260 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ_H 1.56 (s, 6H); 6.95 (d, J = 8.4 Hz, 4 H); 7.09 (d, J = 8.4 Hz, 4H); 7.16 (d, J = 8.1 Hz, 4H); 7.53 (d, J = 8.4 Hz, 4H).^{13}C NMR (75 MHz, $CDCl_3$): δ_C 32.5, 43.3, 120.4, 122.2, 127.4, 127.7, 138.0, 147.6, 149.9, 151.3, 171.4, 172.7, 174.2. HRMS (EIS-MS) m/z 637.4716 $[M + H]^+$. Anal. Calcl. for $C_{33}H_{22}Cl_2N_6O_4$: C, 62.18; H, 3.48; N, 13.18. Found: C, 61.97; H, 3.71; N, 12.89%.

6. Conclusion

The oxacalixarenes **1**–**10** with bisphenol A unit at the intra annular junction have been successfully synthesized by aromatic nucleophilic substitution through addition elimination process and characterized from spectral and analytical data. The photophysical properties show that the presence of electron donating and electron withdrawing substituents exhibit better molar absorptivity. The oxacalixarenes **7** and **10** show better fluorescence emission with higher λ_{em} values than the other oxacalixarenes. All the oxacalixarenes exhibit quasi-reversible behaviour in cyclic voltammetry due to presence of the electron donating and electron withdrawing substituents with extensive π-conjugation with triazine spacer units.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.tet.2018.04.064.

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