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# A Review on Anthracene and Its Derivatives: Applications

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## Research Article

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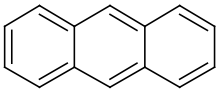
**ABSTRACT**

In this review article, we report applications of anthracene derivatives and the structure-activity relationships of these compounds. The anthracene chromophore plays a prominent role in the development of organic photochemistry. Anthracene derivatives have been extensively investigated in many fields, e.g., material chemistry, thermochromic or photochromic chemistry and organic light-emitting devices. Moreover, anthracenes have been used in optical, electronic and magnetic switches. In biological systems, anthracene skeletal compounds are also useful for probing DNA cleavage. In medicinal field the anthracene derivatives act as good anti-cancerous drugs and they are carcinogenic to many living beings.

## INTRODUCTION

### A Brief History of Anthracene

Anthracene is a solid polycyclic aromatic hydrocarbon consisting of three fused benzene rings. During the course of his studies on solid hydrocarbons that were obtainable from coal tar by distillation, Fritzache discovered in 1866 that saturated solutions of anthracene upon exposure to sunlight gave a colorless crystalline precipitate which regenerated anthracene upon melting. The hydrocarbon played a modest role in the development of structural theory. Anthracene is mainly converted to anthroquinone, a precursor to dyes. In 1901, Bohn discovered the remarkable condensation undergone by aminoanthraquinone, leading to the formation of indanthrene and flavanthrene. Thus anthracene, now approaching its centenary still provides abundant material for scientific investigation and practical application.



**Anthracene**

### Research on Anthracenes and Their Derivatives

Anthracenes are known to have significant biological activities against L1210 *in vitro* tumor cells [1]. Pseudourea was one of the earliest examples of anthracene-based drugs tested in clinical trials [2] and anthracene itself was reported to be effective against specific skin ailments [3]. The planar, linear, three-ring system of the anthracene nucleus has potential for overlapping with the DNA base pairs [4]. The versatile chemistry of anthracene nucleus provides a convenient route to prepare a number of closely related derivatives [5].

Anthracene probes absorbs moderately in the near-UV region and good gives fluorescence quantum yields, which are useful to monitor ligand binding to DNA by spectroscopic methods [6]. The GC sequences of DNA quench the fluorescence of anthracene derivatives, AT sequences enhance anthryl fluorescence, and this provides a useful marker to identify the nature of the binding

site [7]. Anthryl probes have long-lived triplet excited states, which can be used to induce significant DNA damage and strand cleavage [8-10]. Substituents at the 9 and 10 positions of the anthracene nucleus are strategically positioned such that these occupy the grooves when the anthracene moiety is intercalated into the helix [11]. The anthracenedione moiety is also known to undergo redox processes, which could directly produce cytotoxic effects [12]. There are four naturally occurring anthracenes viz. 1,4,10-trimethoxyanthracene-2-carbaldehyde, (1,4,10-trimethoxy-2-anthracen-2-yl) methanol, 1,4,8,10-tetramethoxyanthracene-2-carbaldehyde, 1,4,10-trimethoxyanthracene-2-carboxylic acid and 1,3-dimethoxy-2-methoxymethylanthraquinone, which were extracted from a woody plant *Coussarea macrophylla* [13].

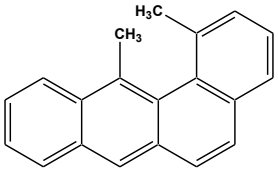
Yu et al. reported the bis anthryl compound and its DNA binding and cleavage studies. The bis anthryl compound shows more binding constant than the mono anthryl compound [14]. Tolpygin has reported the photo induced electron transfer effect in the amino methyl anthracene derivatives. The amino methyl anthracene derivatives could give rise to photo-induced electron transfer in the excited state from lone pair on nitrogen atom to the anthracene fragment, which leads quenching of fluorescence in the latter. Interaction of such compounds with metal cations or proton inhibit photo-induced electron transfer, thus inducing strong fluorescence of the sensor [15]. Kraicheva reported the biological activities of anthracene with amino phosphonic acids. These are quite promising as anticancer agents. Anthracene derived amino phosphonates might be of particular interest in this direction taking into account that the DNA intercalating anthracene ring is the main pharmacophoric fragment of some cytostatic drugs [16]. Phanstiel et al. reported the anthracene containing polyamine compounds. These compounds show a selective drug delivery (cell surface protein) [17]. Metal-free DNA cleaving reagents have been studied by Gobel and co-workers, these compounds are thought of as safer agents for cleaving the P-O bond of phosphodiesters in nucleic acids, showing clinical potential [18]. Small organic molecules, such as guanidinium derivatives [19], cyclodextrin derivatives [20], dipeptides [21] and especially macrocyclic polyamines [22], have also been used as cleaving agents of nucleic acids. The anthraquinone group, as a fine intercalator of DNA, has been frequently adopted in certain anticancer drugs, such as doxorubicin, anthracyclines, mitoxantrone and anthrapyrazoles [23]. Teilla et al. reported that the compound formed by conjugating the cis, cis-triaminocyclohexane-$Zn^{2+}$ complex (cleaving moiety) with anthraquinone (intercalating moiety) via an alkyl spacer led to a 15-fold increase in DNA cleavage efficiency when compared with the cis, cis-triaminocyclohexane- $Zn^{2+}$ complex without the anthraquinone moiety [24].

Yu et al. reported that macrocyclic polyamine bis-anthracene conjugates showed higher DNA binding and photocleaving abilities than their corresponding mono-anthracene conjugates [14]. Roe et al. showed carcinogenic activity of some benzanthracene derivatives in new born mice [25]. Fabbrizzi et al. explained the redox switching of anthracene fluorescence through the CuII/CuI Couple. Lorente et al. reported concentration dependent interaction studies with DNA and anthracene derivatives [26].

## APPLICATIONS

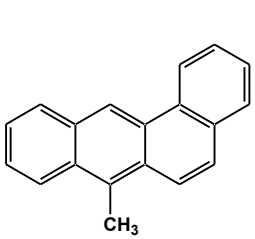
### Carcinogenic Activity

The structure-activity relationships in carcinogenic activity of benzanthracenes have been under study for many years [27]. The fact that 7,12-dimethylbenzanthracene **1** is more active, the strain produced in the molecule by the bulk of the 12-methyl group is responsible. Accordingly, if more strain were introduced more activity might result. Newman et al. synthesized 2, 7, 12-trimethylbenzanthracene, this compound does not exhibit any carcinogenic activity because of the substitution of methyl group in the 1, 2, 3 and 5 position of 7, 12- dimethylbenzanthracene, whereas substitution of methyl group in 4, 6, 9 and 10 position yields active compounds [28].




**1**

Some of the most carcinogenic anthracene based compounds are 7-methylbenzanthracene **2,** 7-bromomethylbenzanthracene **3**, 4-chloro-7-bromomethylbenzanthracene **4**, 7-bromomethyl-12-methylbenzanthracene **5**. Equimolar doses of all these four compounds were injected into the newly born mice; observed that there is increased risk of tumour development compared with that seen in control mice [26].

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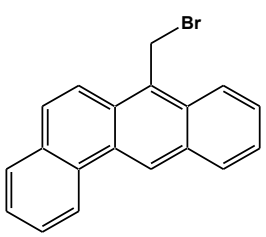


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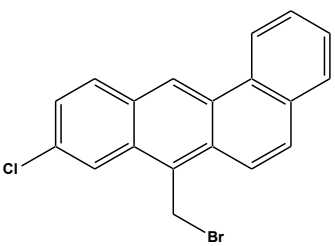


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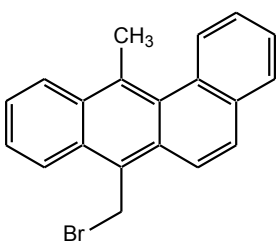


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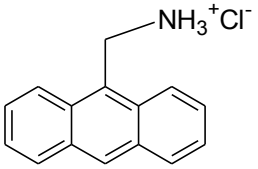
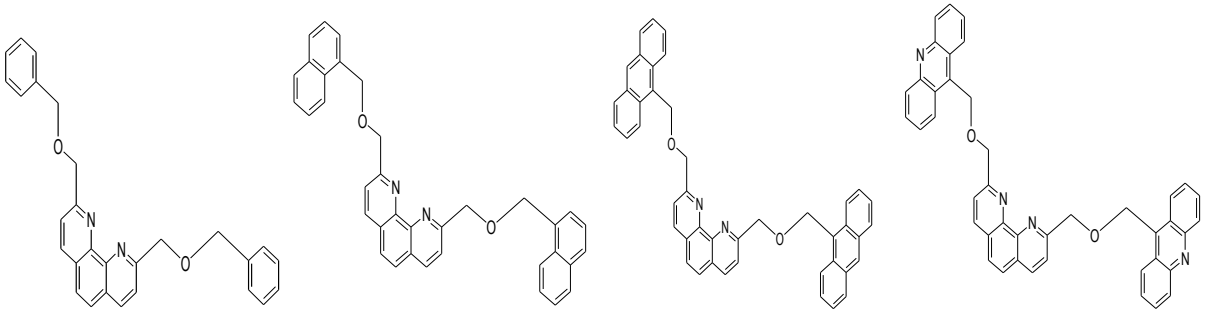
**DNA Photo-cleavage**

The discovery of the nuclease activity of the cuprous complex $(phen)_2$ Cu(I) by Sigman et al. has prompted an intense investigation aimed at establishing the underlying mechanism(s) of the DNA cleavage process [29]. Interesting feature of the anthryl chromophore is its photochemical reactivity and its large singlet excited state energy (76 kcal/mol) which can be used to initiate photoreactions with DNA. Primary alkylamines have been shown to undergo photochemical reactions with nucleotides and cause DNA strand scission. Thus, (9-anthryl) ammonium chloride **6** has a high potential for DNA cleavage studies [30].




6

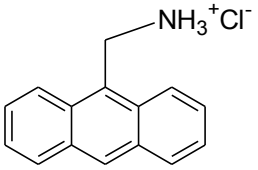
A series of compounds based on 1,10-phenanthroline covalently tethered, at the 2 and 9 positions, to either two benzene **7**, naphthalene **8**, acridine **9** or anthracene **10** chromophores are prepared. Among these acridine and anthracene derivatives were shown to be good DNA photocleavers (pH=7.0, 22°C, 350 nm), whereas benzene and naphthalene were inactive. Acridine compound showed copper(II)-enhanced photocleaving activity at micromolar concentrations, while only 0.25 μM of anthracene derivatives was required to cleave DNA completely. Moreover, the effect of $CuCl_2$ addition to anthracene derivative was shown to be concentration-dependent. Low concentrations of these compounds exhibited cleaving activity that was quenched by addition of the metal salt, while at higher concentrations activity was increased [26].



7 8 9 10

**DNA Binding Studies**

Binding studies of small molecules with deoxyribonucleic acid (DNA) are important in the design of new and more efficient drugs targeted to DNA [31]. It is a quite interesting work to investigate the binding and interactions between small molecules and biomolecules, especially DNA [32]. Because of the important functions of DNA in living organisms, studies towards the interactions between small molecules and DNA will be helpful for preventing and curing diseases [33]. In general planarity was suggested to be one of the important features needed for efficient intercalation into the DNA helix [14]. Therefore the large planar hydrophobic anthryl moiety is expected to facilitate intercalation of the probe into the relatively nonpolar interior of the DNA helix. The methylene chain **11** functions as a short spacer to separate the chromophore and the charge center to above or below the plane of the anthryl moiety. Thus, when the anthryl moiety intercalates into the helix, the cationic charge is positioned closer to the DNA phosphates for a favorable electrostatic interaction. The strong absorption and fluorescence characteristics of the anthryl group provide a sensitive spectroscopic handle to study its interaction with DNA. The well-resolved vibronic transitions of the anthryl chromophore in the 300-400 nm region of the electronic absorption spectrum provide a spectroscopic signature for the probe environment. Changes in the intensities of these transitions can be used to decipher the nature and the strength of the stacking interactions between the chromophore and the DNA bases. Another interesting feature of the anthryl chromophore is its photochemical reactivity and its large singlet excited state energy (76 kcal/mol). These can be used to initiate photoreactions with DNA [30].

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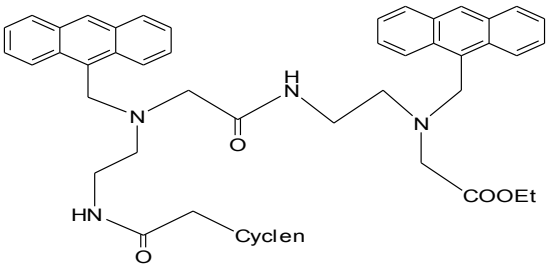
The bis-anthryl compound with multiple peptide band structure backbone, cyclen (1, 4, 7, 10-tetraazacyclododecane) moiety was introduced to enhance water solubility and binding ability towards DNA. The DNA binding activity of **12** was higher compared with the mono-anthryl compound **13** with similar structure found that DNA binding constant of the bis-anthryl compound is 100 times more than that of monoanthryl compound. On the other hand, mono anthryl compound shows significant CG-selective DNA

binding activity [34]. In aqueous solutions, imidazolium anthracene probe exhibited a selective fluorescent quenching effect only with DNA among various anions including the nucleotides investigated. This probe was further applied to monitor the activity of DNase [35].

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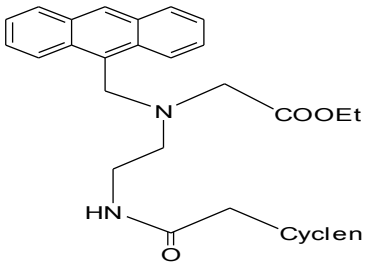


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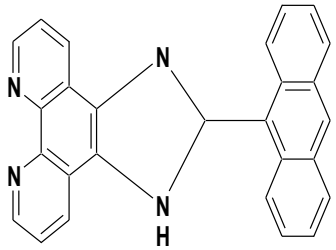
The anthracene **14** and pyrene **15** chromophore appended polypyridyl ligands and their mixed ligands ruthenium complexes are studied with DNA have revealed that these complexes bind to DNA, mainly in an intercalative mode with moderate strengths. Modification of phen, especially extension of the planarity of the ligand and attaching aromatic chromophores(antracene) that will increase the strength of interaction of its complexes with DNA [36].

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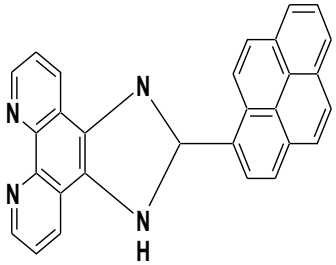


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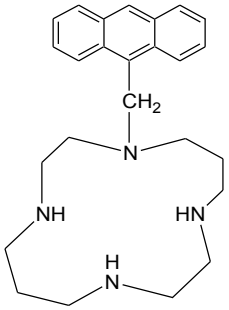
**Redox Activity**

The anthracenes are strong light emitting fragments and chemically stable. The transitoion metal based anthracene appended cyclam rings **16, 17** show a rich and versatile redox activity. Fluorescence quenching can be ascribed to an electron transfer process from the proximate tertiary amine nitrogen atom of the tetraza ring to the excited state of the anthracene fragment [37].

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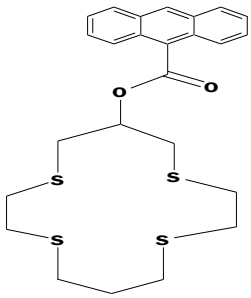


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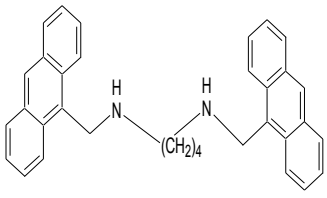
Profatilova et al**.** studied the redox activity of potent chemosensors based on anthryl containing diamines **18**, thiourease **19** and urease **20** in the absence and in the presence of complexing metal cations in solution was studied by cyclic and differential pulse voltammetry. The oxidation of compounds under consideration occur in one or two steps involving the anthryl fragment and the donor moiety i.e., amino, thiourea or urea group. It is known that anthracene is reversibly oxidizes via formation of a stable radical cation. Similar oxidation pattern was reported for chemosensors, 9,10-bis(1,3-dithiol-2-ylidine)-9,10-dihydro anthracene derivatives, in which the sulfur containing ionophore was oxidized at about 0.35 V and the oxidation peak of anthracene moiety was observed at 1.62 V [38]. The oxidation potentials are calculated from Rehm-Weller Equation [39].

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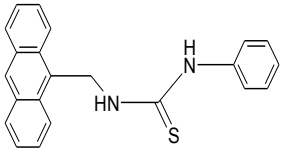


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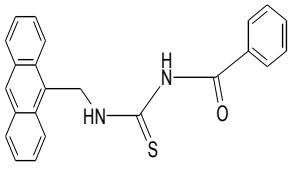


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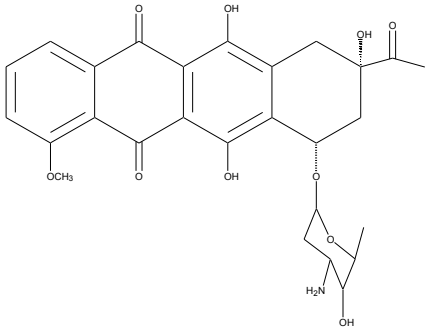
**Anticancer Activity**

Anthracyclines (anthracycline antibiotics) **21** are used in cancer chemotherapy. These anthracyclines inhibit DNA and RNA synthesis by intercalating between base pairs of the DNA/RNA strand, thus preventing the replication of rapidly-growing cancer cells [40]. The anthracenediones represent two latter generation classes of DNA intercalators that show great clinical promise as antitumor drugs [41]. An intermediate, 6-bromomethyl-1,4-anthracenedione **22** was synthesized and converted to various active anti-tumour agents, including a water-soluble phosphate ester pro-drug. Based on their ability to decrease L1210 and HL-60 tumor cell viability, 1,4-dihydroxyanthraquinones **23** are inactive but 1,4-anthracenediones **24** have interesting anti-tumour activity [42].

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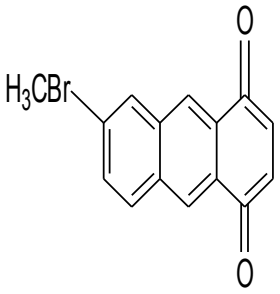


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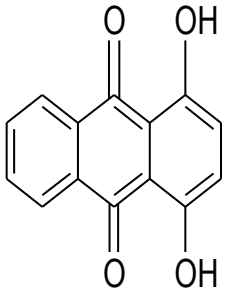


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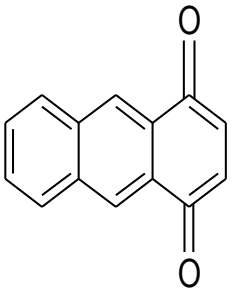


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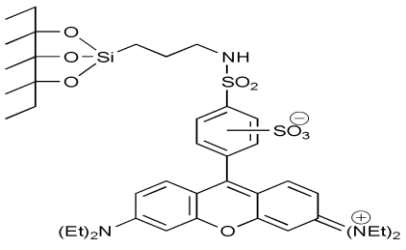
**Chemosensor**

There has been an increasing interest in the recent years in the development and study of chemosensors showing light emitting signal [43]. Different approaches have been followed in the design of chemosensors, most of them involving the coupling of anion binding sites with chromogenic or fluorogenic signaling subunits. However, in most cases colour changes are only observed in non-aqueous solvents such as chloroform or acetonitrile and there are relatively few examples of chemosensors for anion sensing that work in aqueous solution. An alternative method for anion sensing to the anion recognition approach is the use of specific reactions produced by target anions adequately coupled to a signaling event. Ramon et al. described the optical method for fluoride determination in aqueous samples of the specific attack of fluoride onto silica at acidic pH. The silica is used as support for covalent anchoring of chromophores or fluorophores, then, the presence of fluoride in solution implies the destruction of the silica support and the liberation of the organic molecule to the solution. Some of the anthracene **25** derivatives also used in fluoride determination in aqueous samples based specific reaction between fluoride and silica has been developed and applied on real samples [44].

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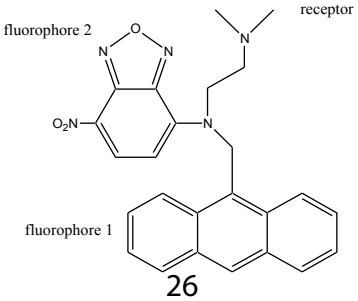
**Fluorescence**

Fluorescence (FL) chemo-/biosensors have received a great deal of attention because of their potential applications in chemistry, materials science, biology, and medicine [45]. Anthracene and its derivatives [46] constitute a very famous class of fluorophores that have been widely used in the development of FL sensors because of their excellent photoluminescence property and chemical stability [47].

Fluorescent chemosensors whose action is based on the PET (photo-induced electron transfer) effect are widely used in the determination of various substances in the environment. Fluorescent systems, which are capable of sensing various chemically, environmentally, and biologically significant species, are of great current interest [48]. A majority of these fluorescent sensors are three-component systems comprising a signaling unit, a guest binding unit, and a linker that connects these two units. The signaling unit, called fluorophore, is responsible for the absorption and emission of light, the guest binding unit, called receptor, is essential for the complexation and decomplexation of the guest, and the linking unit, called spacer, often plays a key role in establishing the electronic communication between the fluorophore and receptor. Compared to the large number of fluorophore-spacer-receptor systems available for sensing alkali and alkaline earth metal ions, only few fluorescent sensor systems for the transition metal ions are described in the literature [49].

Anthracene and 4-amino-7-nitrobenzoxa[1,3]diazole (ANBD) **26** moieties have been chosen as the fluorophore components

because of their distinct absorption and emission features. The fluorescence signaling ability has been examined for several alkali, alkaline earth, transition, and heavy metal salts. In the presence of alkali and alkaline earth metal ions, structure does not show any spectral change. The addition of transition metal salts leads to an enhancement of the emission intensity in the short-wavelength region and simultaneous decrease of the long-wavelength emission intensity. Thus providing a wavelength ratiometric response to transition metal ions [50].

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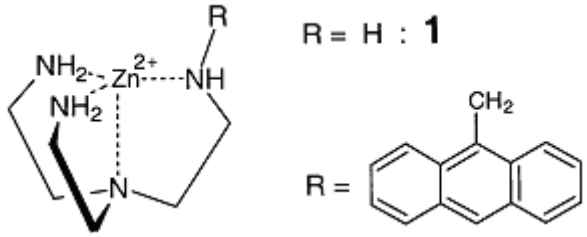
PET fluorescent sensors for anions were first designed by Czarnik et al., using a similar synthetic approach: in this case the receptor was a polyammonium ion and the covalently linked fluorophore was anthracene. The hydrogen bonding interaction between the polyammonium subunit and the anion (e.g., $H_2PO_4^-$) interrupted an operating PET mechanism, thus inducing an enhancement of the anthracene emission [51]. More recently, Lehn and co-workers used more sophisticated cyclic and polycyclic polyammonium receptors to build fluorescent molecular sensors for a variety of anions [52]. Other than hydrogen bonding can be conveniently used for anion recognition and fluorescent sensing the metal–ligand interaction. The $[ZnII(tren)]^{2+}$ complex, (tren: tris(2-aminoethyl) amine) **27** is a useful platform for anion recognition. The metal complex exhibits a trigonal bipyramidal stereochemistry and maintains a vacant axial position, available for the coordination of a further ligand, either a solvent molecule or an anion [53].

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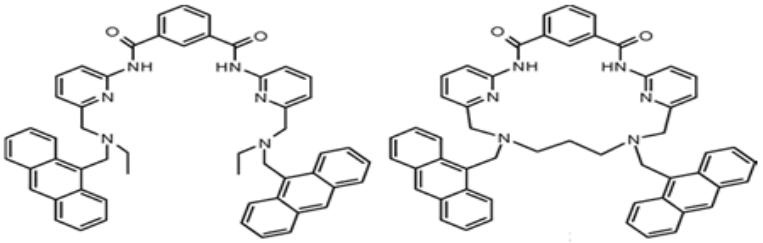
Anthracene based open **28** and macrocyclic **29** receptors acts as fluorescent chemosensors for the detection and sensing of the biologically important substrate urea in the less polar solvent $CHCl_3$, as well as in the more polar solvent $CH_3CN$. The binding constant values determined for urea $1.97 \times 10^6$ having high value compared to urea $1.35 \times 10^6$, the receptors act as good PET sensors [54,55].



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## CONCLUSION

The anthracene chromophore plays a prominent role in the development of organic photochemistry. Anthracene derivatives have been extensively investigated in many fields, e.g., material chemistry, thermochromic or photochromic chemistry, and organic light-emitting devices. Moreover, anthracenes have been used in optical, electronic, and magnetic switches. In biological systems, anthracene skeletal compounds are also useful for probing DNA cleavage. In medicinal field the anthracene derivatives act as good anti-cancerous drugs and they are carcinogenic to many living beings.

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