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Facile synthesis and anion binding studies of fluorescein/benzo-12-crown-4 ether based bis-dipyrromethane (DPM) receptors†

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Two novel fluorescein as well as benzo-12-crown-4 ether functionalized dipyrromethane receptors (**DPM3** and **DPM4**) have successfully been synthesized. The anion (used as their TBA salts) binding studies of thus prepared **DPM3** and **DPM4** receptors were evaluated by the UV-visible spectrophotometric titrations. Binding affinities as well as the stoichiometry were determined through the UV-visible titrations data with the involvement of the BindFit (v0.5) package available online at https://supramolecular.org. Moreover, binding events were validated by means of the comparison of the partial ^{1}H-NMR spectrum of the simple host molecule with that of the host–guest complex, and the 1 : 1 stoichiometry were further confirmed by the Job's method of continuous variation. From the results, we observed the binding constant (K_a) values of **DPM3/DPM4** with various tested anions in the range of 516.07 M^{-1} to 63789.81 M^{-1}, depending upon the nature/shape/size of the anions. Moreover, the anion–π interactions were confirmed by the partial ^{1}H-NMR spectral data, and further supported by the literature reported systems. The authors hope that such types of valued receptors will be benefitted in future for the recognizing/binding of a variety of biologically important anions.

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Introduction

In the past decade, supramolecular chemistry has displayed a promising role by producing a myriad of sensitive as well as selective artificial receptors for recognizing/capturing of various neutral guest molecules or ionic entities (cations, anions and/or ion-pairs), which has enormously revolutionized the host–guest chemistry.[1–5] Notably, scientists worldwide are developing the anion coordination chemistry by presenting a variety of synthetic receptors for the recognition, sensing, and/or extraction of the diverse biologically/environmentally significant polystructural anionic species.[6,7] Although, anions are considered indispensable components for numerous biological systems, as many physiological processes are directly or indirectly controlled in the presence of anions of specific importance.[8,9] However, decrease or increase in the concentrations of the anions from the human body or in the environment causes several diseases including Bartter's syndrome, Pendred's syndrome, cystic fibrosis, dent's disease, osteoporosis, and pollutants linked with the anionic entities are contamination of drinking water, carcinogenesis and eutrophication of rivers *etc*.[10] In this regard, to date, though, a plethora of anionic receptors have fruitfully been developed, exhibiting selectively high affinity towards sensing or recognition of the anions by fabricating changes in the spectroscopic signals.[11–19] But, we believe that, there is still a pressing necessity to develop simple-to-make yet highly sensitive and selective anion receptors.[20–30]

Gratifyingly, preorganization leads to the selective as well as effective binding between the specific receptor and analyte(s). Moreover, it also upturns the rigidity, which usually hinders the entree of analyte towards the binding site(s). This can produce undesirable interruption in the measurement of equilibrium, and also at the same time retard the kinetic measurements, hence the receptor rigidity and flexibility must be kept in a proper balance, while designing the receptor(s) of particular interest. Noticeably, a central requirement for a chemosensors functioning is the reversible binding of receptor to analyte – allowing the concentration of the analyte to be measured at the equilibrium through analytically useful signals. Therefore, while scheming the supramolecular receptors, certain requirements must be kept in mind: (1) choice of chromophore/fluorophore; (2) analyte binding site(s); (3) immobilized methods and optical signaling mechanism; (4) preorganization characteristics; (5) lastly, the composed flexibility as well as the rigidity.[28,31,32]

Undoubtedly, the design and construction of anion receptors is highly challenging because of: (1) diverse geometries/shapes

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† Electronic supplementary information (ESI) available: The original ^{1}H-NMR, ^{13}C-NMR, HRMS of all the synthesized compounds are available in ESI. The UV-vis titration of receptor with anions in CH_3CN. Snapshot capture of Bindfit plots for receptors and anion titration, displaying 1 : 1, 1 : 2 and 2 : 1 stoichiometry utilizing Nelder–Mead fit are available in ESI. See DOI: https://doi.org/10.1039/d3ra05171d

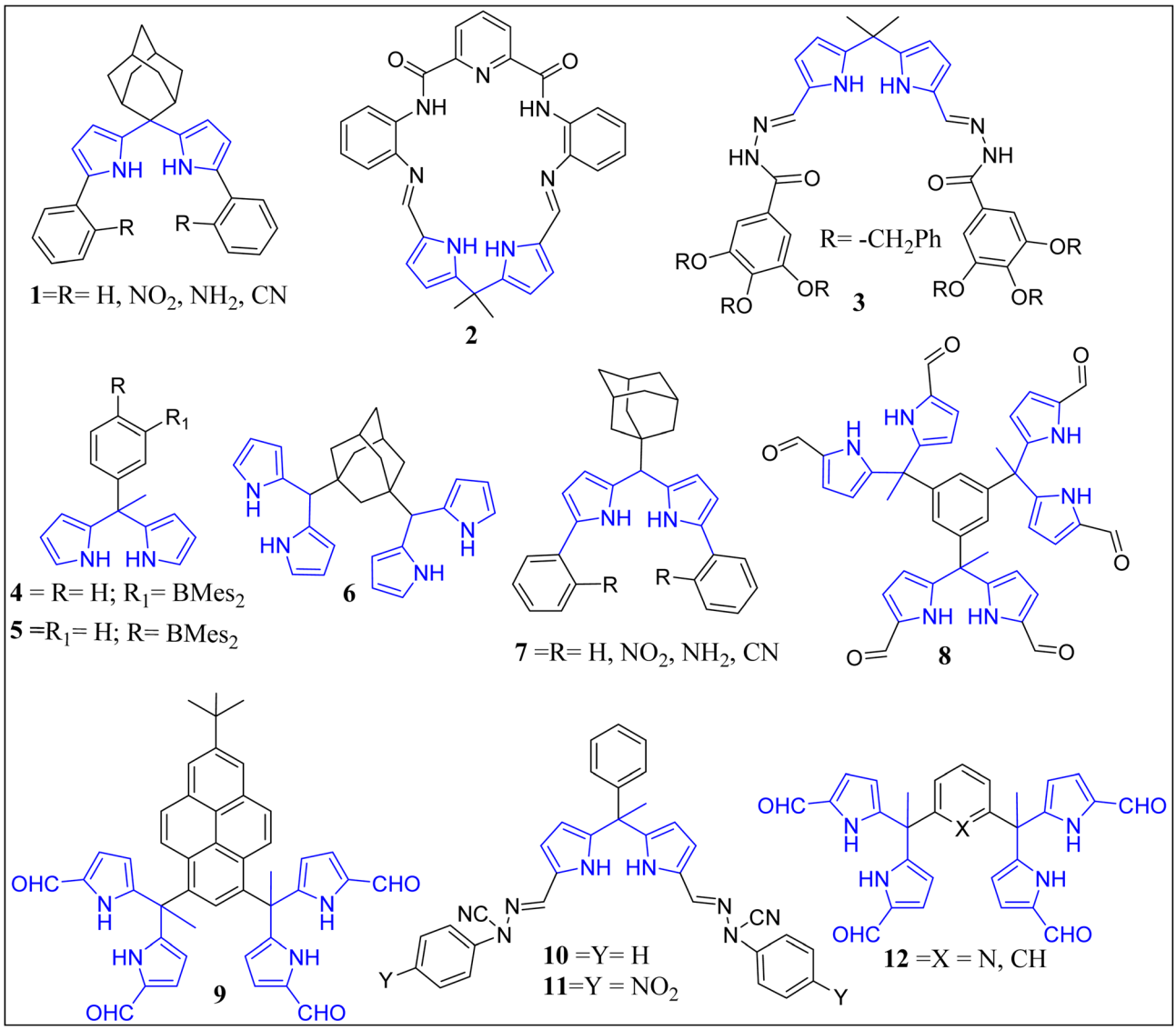
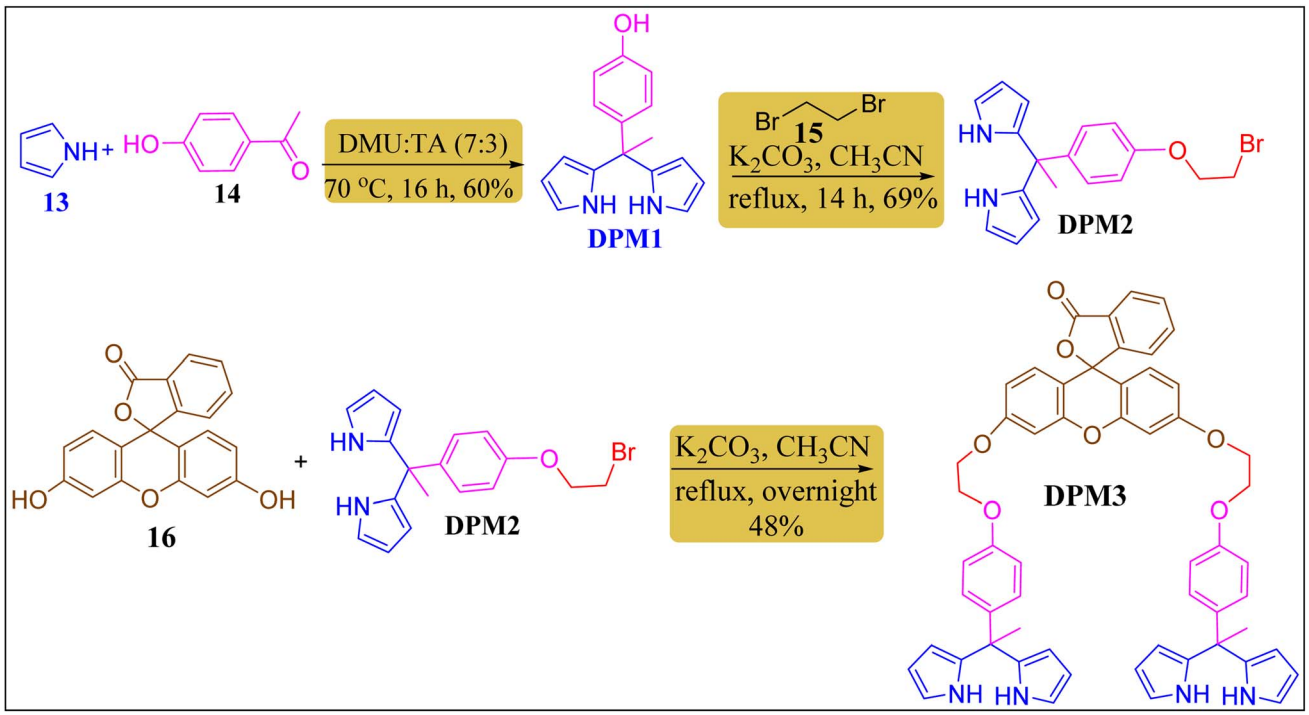


Fig. 1 A list of already reported DPMs by different research groups for anion binding.

of the anions; (2) their large size-to-charge ratio; (3) and the higher hydration/solvation energies of the anions as compared to the cationic receptors. Generally, a combination of non-covalent/supramolecular interactions participates in the anion recognition chemistry, including coulombic interactions, halogen bonding, hydrogen bonding, CH–anion, anion–π interactions, π–π stacking, and other important non-covalent forces, as well.[33–46] However, most frequent moieties consisting of the active hydrogen bonding sites for instance urea, thiourea, phenol, amide, pyrrole *etc*., have prominently been used for the design and synthesis of the anion receptors.[47–52] Remarkably, as can be inspected from the Fig. 1, by utilizing the hydrogen bonding sites of pyrrolic systems, Sessler's research group has reported that receptors **8** & **12**, displayed high affinity towards the biologically important dihydrogenphosphate and pyrophosphate anions (used as their tetrabutylammonium salts) in chloroform solvent.[53–55] On the other hand, the same research group has also revealed the selective binding of tetrabutylammonium dihydrogen phosphate over other tested anionic salts with the pyrene-functionalized *tetrakis*-(1*H*-pyrrole-2-carbaldehyde) (**9**) in $CHCl_3$.[56] Similarly, Bao and co-workers have reported two novel tweezer-like receptors, namely, the 2,2′-bis(2-cyano-2-phenylvinyl)-5,5′-dimethyl dipyrromethene (**10**) and 2,2′-bis[2-cyano-2-(4-nitrophenyl)vinyl]-5,5′-dimethyl dipyrromethane (**11**), displaying strong and selective binding towards dihydrogenphosphate and fluoride anions (Fig. 1).[57] In a separate report, Zuo and teammates have described a selective optical and electrochemical sensing of the fluoride anion with the usage of tetrathiafulvalene (TTF) based boron-dipyrromethene receptor through ^{1}H-NMR titration, which was further supported by virtue of the Density Functional Theory (DFT) calculations.[58] On the other occasion, Sessler's team has also achieved worthy outcomes with bipyrrole and dipyrromethane appended amido-imine hybrid macrocycles, toward oxoanions in acetonitrile.[59] On the other hand, Ustynyuk's group has reported impactful results of anion binding



Scheme 1 Synthesis of the fluorescein-based bis-dipyrromethane **DPM3**.

studies using polypyrrolic 2,5-diamidothiophene Schiff base with 1.2 : 1 hydrogen sulfate anions *versus* nitrate selectivity in flexible dipyrromethane, whereas rigid congener displayed 7.4 : 1 selectivity towards hydrogen sulfate.[60]

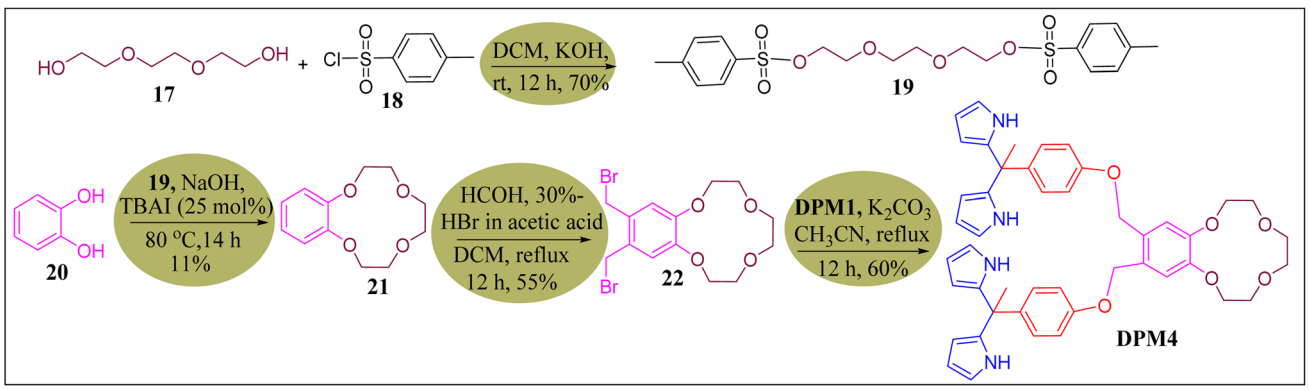
Fluorescein and its congeners have a potential future as fluorescent probes for diverse analytes as well as bio-labeling reagents. Additionally, exhibiting outstanding fluorescence quantum yields and other photophysical characteristics, such as the capacity to emit and absorb light at extended wavelengths and have great light stability.[61–65] On the other hand, crown ethers, cyclic compounds containing various ether groups, displaying strong binding towards cations by forming complexes. Crown ethers exhibiting extinction coefficients and are mostly used for phase transfer catalysis, synthesis of ion/ion pair receptors, biological/pharmacological applications, and mechanically interlocked supramolecular systems.[66–69]

Therefore, bearing the importance of fluorescein, crown ethers and dipyrromethenes (DPMs) containing receptors in mind, in addition to further extend our work on the DPM-based systems,[70] herewith we envision to construct two novel dipyrromethane receptors (**DPM3** and **DPM4**), to investigate their anion binding affinities. We are in the opinion that these newly developed receptors, may open several hidden opportunities for the young researchers, to further advanced the arena of molecular recognition/sensing in many years to come.

Results and discussion

Synthesis and characterization

Towards the construction of our targeted dipyrromethane receptors (**DPM3** and **DPM4**), we embarked with the preparation of **DPM1** through the condensation reaction of easily available



Scheme 2 Synthesis of the benzo fused 12-crown-4 based bis-**DPM4** from catechol and **19**.

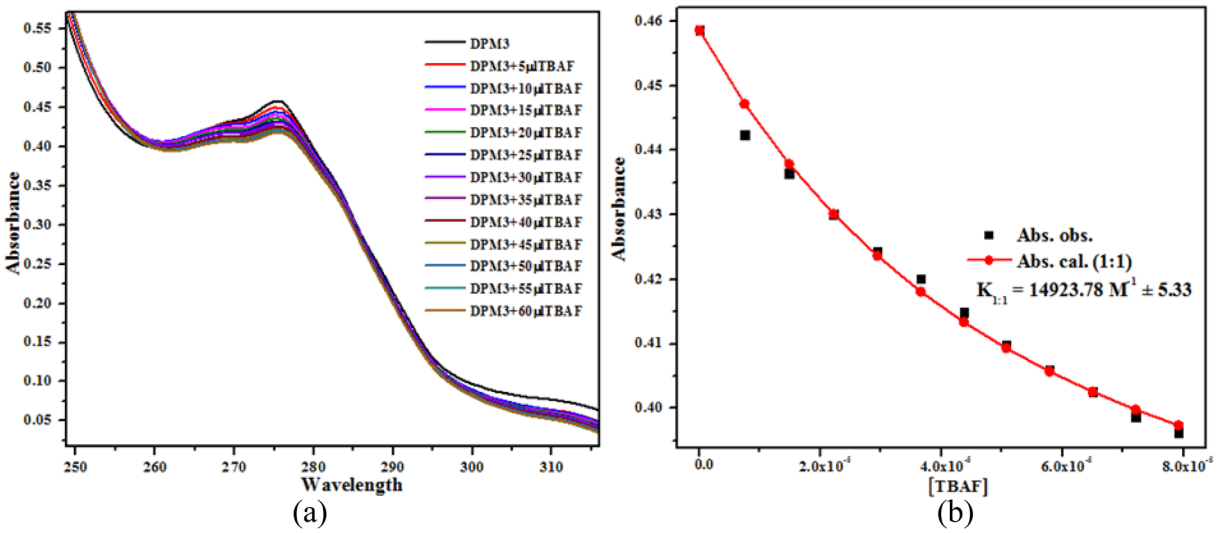


Fig. 2 The UV-vis titration of **DPM3** with **TBAF** in CH_3CN (a), and binding isotherm fitting of thus obtained data using online Bindfit v0.5 program (b).

pyrrole (**13**) and *p*-hydroxyacetophenone (**14**) under a low melting deep eutectic mixture, using our earlier reported protocol (Scheme 1).[70] Later, the **DPM1** was converted into the long-tailed ether based **DPM2** in good yield (69%) by refluxing it with 1,2-dibromoethane (**15**) in the presence of K_2CO_3/MeCN for overnight. Next, **DPM2** was treated with the parent fluorescein (**16**) using K_2CO_3 in refluxing acetonitrile to furnish the desired **DPM3**.

On the other hand, synthesis of the **DPM4** was achieved from the commercially available *tri*-ethyleneglycol (**17**), *p*-toluenesolfunyl chloride (**18**), and the catechol (**20**). In this regard, first we prepared the ditosylated compound (**19**) by reacting **17** with **18** using KOH in dichloromethane (DCM), which was then treated with catechol (**20**) in the presence of NaOH to yield the benzo-12-crown-4 ether (**21**) in low yield (Scheme 2). Furthermore, the reaction of benzo-12-crown-4 (**21**) with

Table 1 Binding constant values of **DPM3** and **DPM4** receptors with various test anions[a]

S. no	Anion	**DPM3** (K_a, M^{-1})	**DPM4** (K_a, M^{-1})
1	F^-	14923.78 (±5.33)	63789.81 (±9.87)
2	Cl^-	12616.17 (±1.63)	12670.68 (±4.78)
3	Br^-	5527.42 (±2.70)	8644.5 (±9.96)
4	I^-	ND	ND
5	NO_3^-	1900.37 (±0.38)	3640.14 (±1.77)
6	SCN^-	NA	516.07 (±1.38)
7	AcO^-	6018.41 (±3.95)	12935.35 (±4.09)
8	$H_2PO_4^-$	ND	1838.17 (±1.98)
9	HSO_4^-	2825.47 (±1.17)	2121.77 (±0.50)

[a] K_a values, calculated using the Bindfit software through 1 : 1 binding model. The errors are in parenthesis with <10%, [**DPM3** and **DPM4**] = 5.0×10^{-6} M, [anions TBA salts] = 1.5×10^{-4} M at $T = 32$ °C ± 2 °C. ND = not detectable.

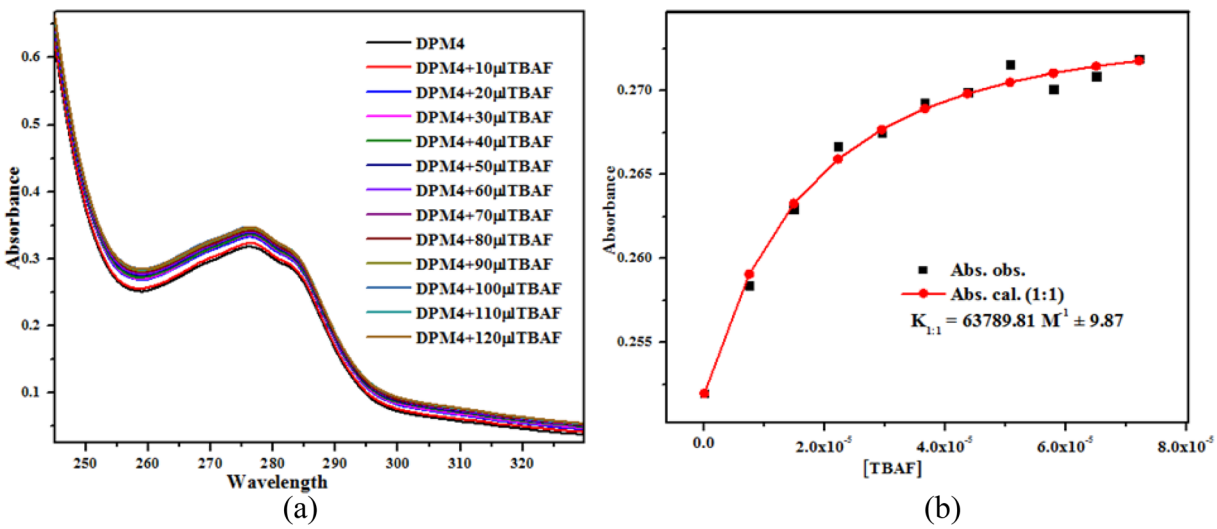


Fig. 3 The UV-vis titration of **DPM4** with **TBAF** in CH_3CN (a), and binding isotherm fitting of thus obtained data using online Bindfit v0.5 program (b).

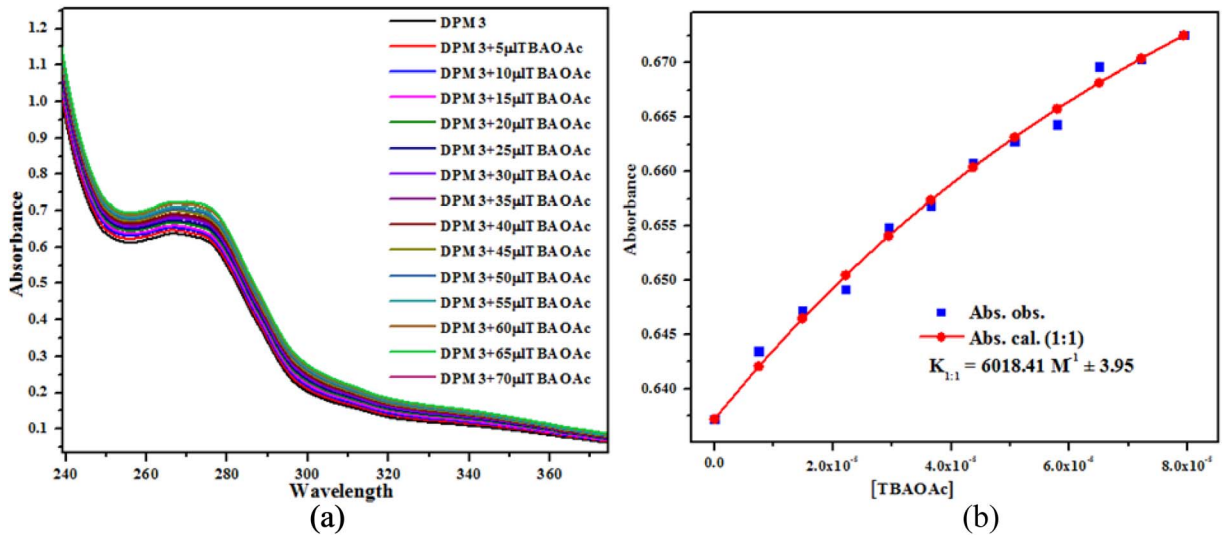


Fig. 4 The UV-vis titration of **DPM3** with **TBAOAc** in CH_3CN (a), and binding isotherm fitting of thus obtained data using online Bindfit v0.5 program (b).

paraformaldehyde and HBr in DCM afforded the 4,5-dibromomethyl benzo-12-crown-4 (**22**) in 55% yield. Next, the compound **22** was treated with the **DPM1** to provide the anticipated **DPM4** in respectable yield (Scheme 2). Thus, prepared DPM receptors were characterized and identified by means of NMR spectroscopy and mass spectrometry (see ESI†).

Anion binding studies through UV-vis titrations

After successful synthesis and characterization of the targeted **DPM3/DPM4** (5.0×10^{-6} mol L^{-1}), next we performed the UV-vis titration experiments using them with a variety of anions for example, HSO_4^-, NO_3^-, SCN^-, AcO^-, $H_2PO_4^-$, F^-, Cl^-, Br^-, and I^-, used in the form of their tetrabutylammonium salts (1.5×10^{-4} mol L^{-1}) in CH_3CN solvent. Both the newly synthesized bis-dipyrromethanes *i.e.*, **DPM3** and **DPM4**, displayed maximum spectral change in complex (anion + receptor) form (increase in absorbance by increasing the concentration of guest), and different binding affinities with the test anions. Towards the first stage of the experiment, UV-vis spectra of the free **DPM3** and **DPM4** (5.0×10^{-6} M) in MeCN solution was recorded, then the guest molecule TBAF (1.5×10^{-4} M) was added in portionwise (5 μL and 10 μL) till the saturation established. From the inspection of the Fig. 2a, it can clearly be seen that the spectra of **DPM3** and **DPM4** showed the bands with maximum wavelength at *ca.* 275 nm, and 277 nm respectively. Noticeably, upon successive addition of 5 μL of TBAF to

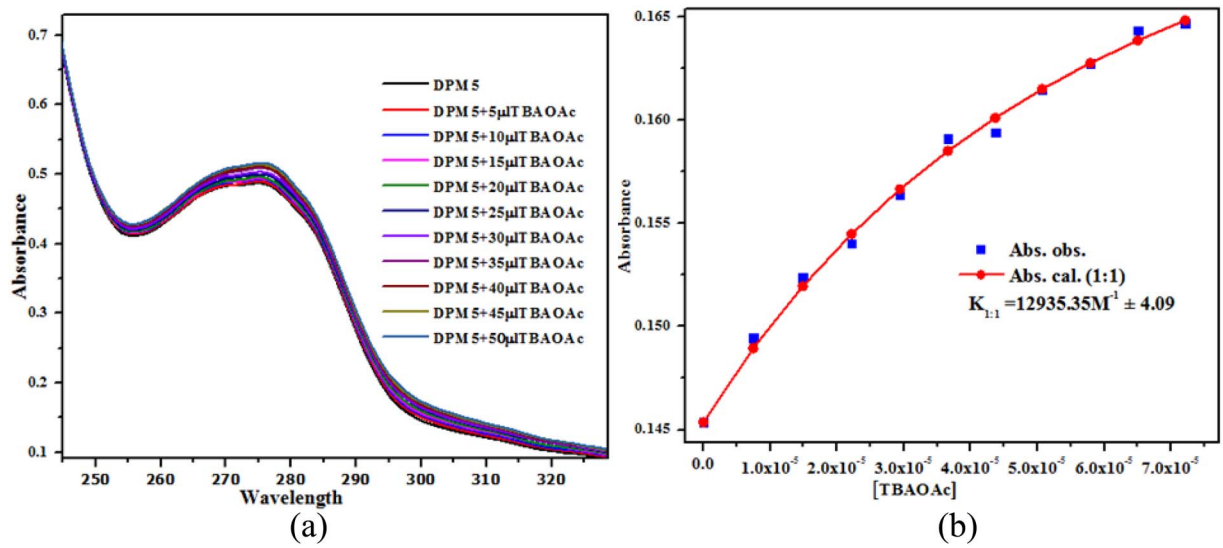


Fig. 5 UV-vis titration of receptor **DPM4** with **TBAOAc** in CH_3CN (a), and binding isotherm fitting of UV-vis titration data by using Bindfit v0.5 program (b).

DPM3, the decrease in the absorbance values were observed at 275 nm. Whereas, upon the successive addition 10 μL TBAF to **DPM4**, the increase in the absorbance values was observed at 275 nm, which continues till the saturation point is obtained (Fig. 2a and 3a). Data obtained were fitted in the Bindfit v0.5 software at 275 nm and 258 nm, respectively for the **DPM3** and **DPM4** with the fluoride anion, the 1 : 1 stoichiometry were observed for both the receptors with the binding constant values of $K_{1:1}$ 14923.78 M^{-1} and 63789.81 M^{-1}, respectively (Fig. 2 and 3). Moreover, the linear acetate anion also showed good results with both the receptors, stoichiometry (1 : 1) and binding constants $K_{1:1} = 6018.41\ M^{-1}$ for **DPM3@AcO**$^-$ and $K_{1:1} = 12935.35\ M^{-1}$ for **DPM4@AcO**$^-$ (<5% error). The stoichiometry and binding constant values of the bis-dipyrromethanes with various other tested anions were calculated in similar manner, using Nelder–Mead fit method from online supramolecular Bindfit v0.5 software (see ESI†). From the calculations of the binding constants ($K_{1:1}$, $K_{1:2}$, and $K_{2:1}$), we observed that the in all the cases, the 1 : 1 stoichiometry was obtained with satisfied value of $K_{1:1}$ within error <10, whereas for the data fitting to 1 : 2, and 2 : 1 stoichiometry, negative or unsatisfied values with more errors were observed (Table 1). Noticeably, similar results were obtained by Pakkirisamy and co-workers with various dipyrromethane towards different anions using UV-vis, fluorescence, NMR spectroscopy besides the DFT studies.[71] On the other hand, Ganguly's and Majerski's research groups, independently, have reported similar studies using different dipyrromethane receptors with varied anions (Fig. 4 and 5).[72,73]

^{1}H-NMR interpretation and the Job's method of continuous variation

To further support the results of UV-vis spectroscopy, obtained from the online supramolecular Bindfit program, partial ^{1}H-NMR spectra of the **DPM3** and **DPM4** were compared with that of the complexed ones (**DPM3**/**DPM4**@TBAF). From the inspection of the Fig. 6, it could be clearly noticed that a peak at 10.37 ppm, attributed to the pyrrolic NH-protons, and the peaks in the range of 8.20–6.55 ppm relates to the aromatic protons, whereas the signals appeared *ca.* at 5.89 ppm and 5.58 ppm belongs to the beta-pyrrolic protons. From the spectrum of the complexed one (**DPM3@F**$^-$), it could be seen that the pyrrolic

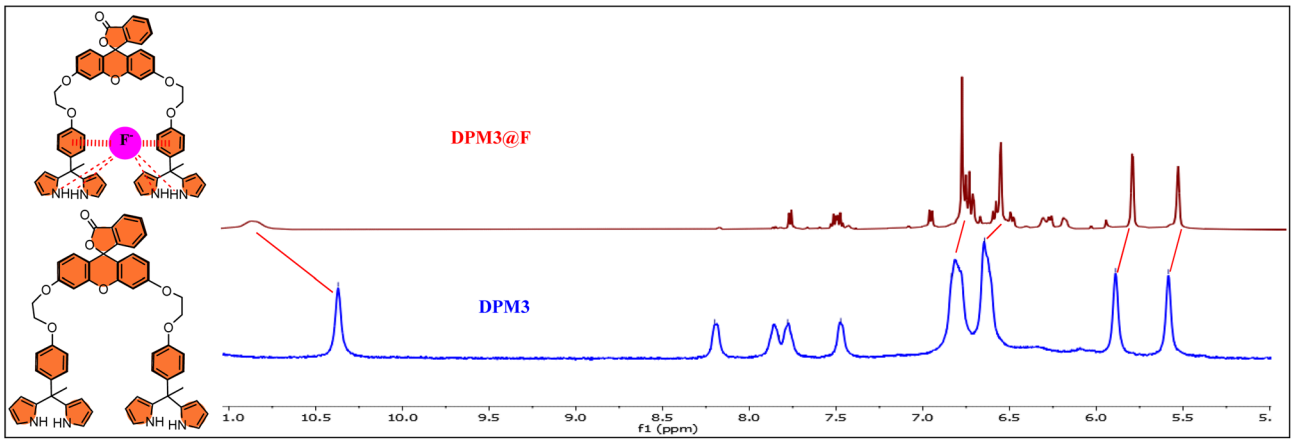


Fig. 6 Comparative ^{1}H-NMR spectra of **DPM3** receptor and complex form (**DPM3@F**$^-$) recorded in the recorded in DMSO-d^6 solvent.

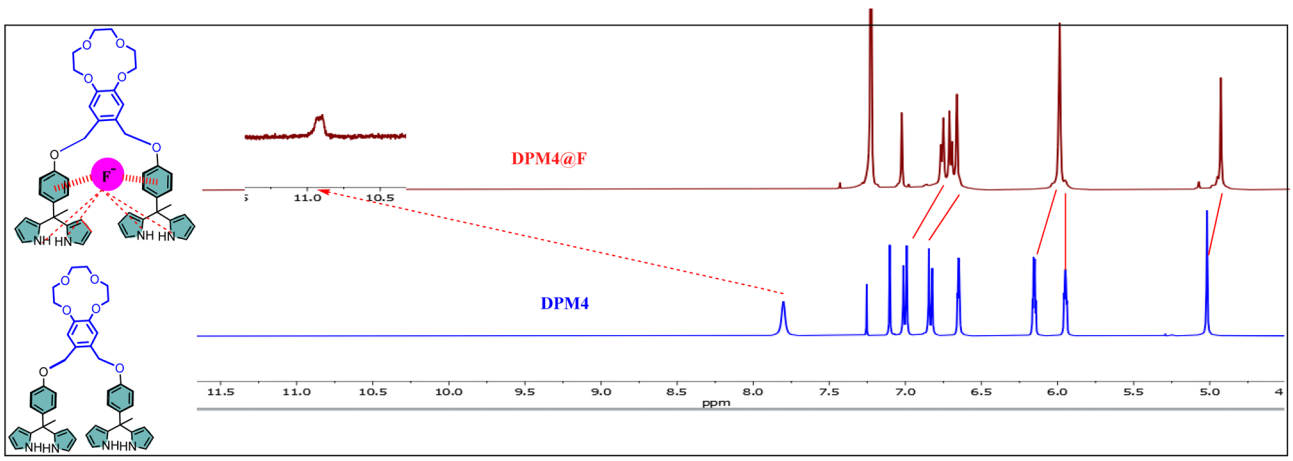


Fig. 7 ^{1}H-NMR spectra of **DPM4** & complex (**DPM4@F**$^-$) recorded in $CDCl_3$ solvent.

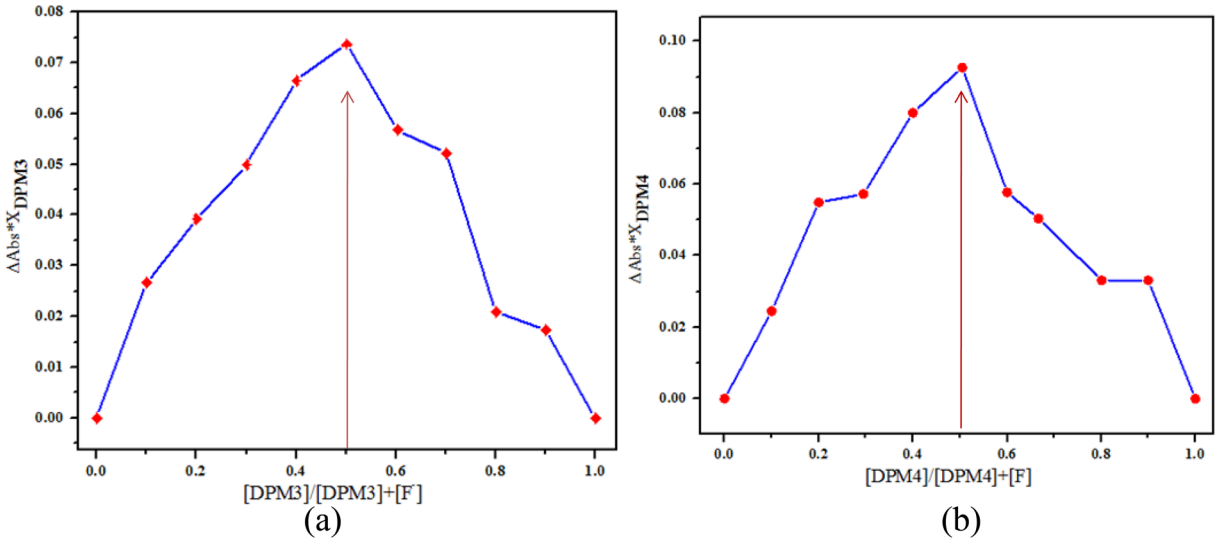


Fig. 8 Job's plot of DPM3 & DPM4 with TBAF in acetonitrile at ambient temperature.

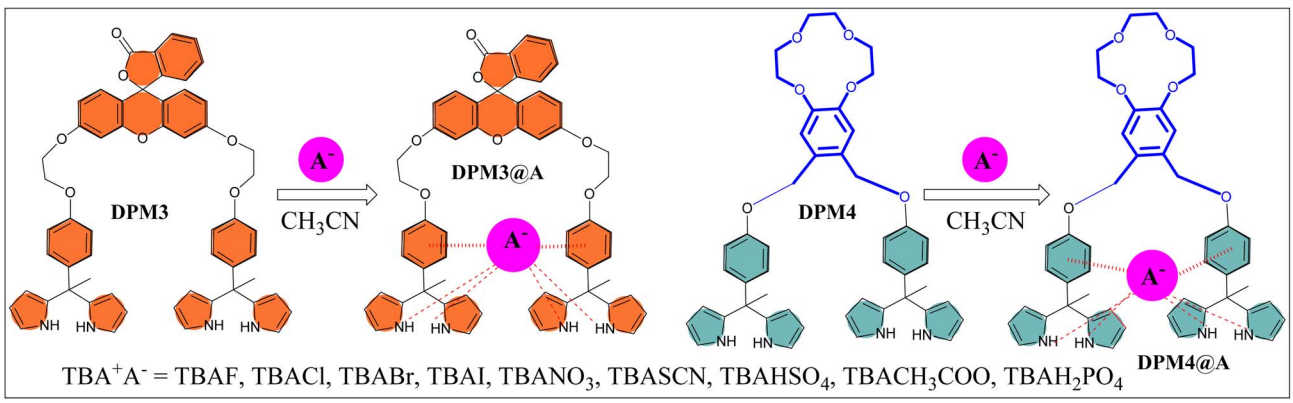


Fig. 9 The probable complex structures of the novel bis-dipyrromethane receptors DPM3 and DPM4 with different anions in 1 : 1 stoichiometric ratio.

N–H protons shifts downfield from 10.37 ppm to 10.87 ppm with $\Delta\delta = 0.50$ ppm, whereas the aromatic ring protons as well as the beta-pyrrolic protons moved towards upfield. Therefore, it could be pointed out that the **DPM3** binds with fluoride anion through both NH-anion as well as anion–π interactions (Fig. 6). On the other front, it could be inspected from the Fig. 7 that in the case of the **DPM4**, pyrrolic N–H protons largely shift towards the low field (downfield) *i.e.*, from 7.80 ppm to the 10.83 ppm ($\Delta\delta = 3.03$ ppm) (Fig. 6). Herein, it was observed that the overall binding constants results were obtained from combination of four N–H-anion hydrogen bonding as well as through anion–π interactions (Fig. 7).[74–77]

The Job's method of continuous variation was performed to authenticate the stoichiometric results acquired from the online Bindfit v0.5 software for **DPM3**@anions and **DPM4**@anions. In this method, the titration was performed between the host molecule (**DPM3** & **DPM4**) and guest molecule (fluoride & acetate) in acetonitrile solution at ambient temperature. However, the concentrations of both the host and guest molecules were held constant (5.0×10^{-6} M), whereas their mole fractions were varied. Furthermore, the graph was plotted between change in the absorption at λ_{max} and the mole fraction of **DPM3/DPM4** *vs.* the mole fraction of **TABF-DPM3** or **TABF-DPM4**. From the inspection of the Fig. 8, it was confirmed that the complex concentration of **DPM3@F**$^-$ and **DPM4@F**$^-$ appeared maximum at value 0.5, thereby confirming the 1 : 1 host–guest complex formation. Along similar lines, for **DPM3@CH$_3$COO**$^-$ as well as **DPM4@CH$_3$COO**$^-$, we noticed the 1 : 1 stoichiometry (see ESI†). From the results of various techniques such as UV-vis titrations, Bindfit v0.5 program, ^{1}H-NMR analysis, and Job's plot, 1 : 1 stoichiometry is confirmed besides the N–H···anions (H-bonding) and anion–π interactions (Fig. 9).

Conclusions and future prospects

Two novel fluorescein and benzo-12-crown-4 ether based dipyrromethane receptors **DPM3** and **DPM4** were successfully

synthesized, and evaluated for anion-binding assay through UV-vis spectrophotometric titrations. The binding constants of both the **DPM3** and **DPM4** with different anions were determined in acetonitrile using online supramolecular Bindfit v0.5 program, displaying 1 : 1 stoichiometry for all the examined anions, were further valuated by Job's plots. The comparative study of ^{1}H-NMR spectra revealed that the anions are captured through both hydrogen bonding and anion–π interactions. The ion-pair studies of these **DPMs** are underway, and will be published in due course. Moreover, benzo-12-crown-4 ether in addition to other higher analogous crown ethers based strapped calix[4]pyrroles (C4Ps) are also under investigations, and will be published shortly. Hopefully, these outcomes will guide to the researchers to develop even more interesting crown ether-based systems for varied applications in future studies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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References

1 I. V. Kolesnichenko and E. V. Anslyn, *Chem. Soc. Rev.*, 2017, **46**, 2385–2390.
2 D.-X. Wang and M.-X. Wang, *Acc. Chem. Res.*, 2020, **53**, 1364–1380.
3 X. Ma and Y. Zhao, *Chem. Rev.*, 2015, **115**, 7794–7839.
4 A. D. O'Donnell, S. Salimi, L. R. Hart, T. S. Babra, B. W. Greenland and W. Hayes, *React. Funct. Polym.*, 2022, **172**, 105209.
5 U. Lüning, *Angew. Chem., Int. Ed.*, 2013, **52**, 4724.
6 P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 486–516.
7 S. Kubik, *Chem. Soc. Rev.*, 2010, **39**, 3648.
8 J. R. Knowles, *Annu. Rev. Biochem.*, 1980, **49**, 877–919.
9 D. Markovich, *Physiol. Rev.*, 2001, **81**, 1499–1533.
10 J. Han, L. Kiss, H. Mei, A. M. Remete, M. Ponikvar-Svet, D. M. Sedgwick, R. Roman, S. Fustero, H. Moriwaki and V. A. Soloshonok, *Chem. Rev.*, 2021, **121**, 4678–4742.
11 K. Bowman-James, *Acc. Chem. Res.*, 2005, **38**, 671–678.
12 *Anion Coordination Chemistry*, ed. K. Bowman James, A. Bianchi and E. García España, Wiley, 2011.
13 S. O. Kang, M. A. Hossain and K. Bowman-James, *Coord. Chem. Rev.*, 2006, **250**, 3038–3052.
14 B. a Moyer, D. A. Bostick, C. J. Fowler, H.-A. Kang, A. Ruas, L. H. Delmau, T. J. Haverlock, J. M. Llinares, A. Hossain, S. O. Kang, K. Bowman-James, J. A. Shriver, M. Marquez and J. L. Sessler, *Supramolecular Chemistry of Selective Anion Recognition for Anions of Environmental Relevance*, 2005.
15 E. García-España, P. Díaz, J. M. Llinares and A. Bianchi, *Coord. Chem. Rev.*, 2006, **250**, 2952–2986.
16 T. Clifford, A. Danby, J. M. Llinares, S. Mason, N. W. Alcock, D. Powell, J. A. Aguilar, E. García-España and K. Bowman-James, *Inorg. Chem.*, 2001, **40**, 4710–4720.
17 A. Bencini, A. Bianchi, E. Garcia-Espana, M. Giusti, S. Mangani, M. Micheloni, P. Orioli and P. Paoletti, *Inorg. Chem.*, 1987, **26**, 3902–3907.
18 A. Schaly, R. Belda, E. García-España and S. Kubik, *Org. Lett.*, 2013, **15**, 6238–6241.
19 L. Rodríguez, J. C. Lima, A. J. Parola, F. Pina, R. Meitz, R. Aucejo, E. Garcia-España, J. M. Llinares, C. Soriano and J. Alarcón, *Inorg. Chem.*, 2008, **47**, 6173–6183.
20 P. A. Gale, E. N. W. Howe and X. Wu, *Chem*, 2016, **1**, 351–422.
21 P. A. Gale and C. Caltagirone, *Chem. Soc. Rev.*, 2015, **44**, 4212–4227.
22 S. A. Wagay, M. Alam and R. Ali, *J. Mol. Struct.*, 2023, 135982.
23 N. Busschaert, C. Caltagirone, W. Van Rossom and P. A. Gale, *Chem. Rev.*, 2015, **115**, 8038–8155.
24 N. Kaur, G. Kaur, U. A. Fegade, A. Singh, S. K. Sahoo, A. S. Kuwar and N. Singh, *TrAC, Trends Anal. Chem.*, 2017, **95**, 86–109.
25 A. Pal, M. Karmakar, S. R. Bhatta and A. Thakur, *Coord. Chem. Rev.*, 2021, **448**, 214167.
26 A. Borissov, I. Marques, J. Y. C. Lim, V. Félix, M. D. Smith and P. D. Beer, *J. Am. Chem. Soc.*, 2019, **141**, 4119–4129.
27 M. J. Langton, C. J. Serpell and P. D. Beer, *Angew. Chem., Int. Ed.*, 2016, **55**, 1974–1987.
28 X. Wu, A. M. Gilchrist and P. A. Gale, *Chem*, 2020, **6**, 1296–1309.
29 G. M. Romano, M. Savastano, C. Bazzicalupi, R. Chelli, V. Lippolis and A. Bencini, *Dalton Trans.*, 2023, **52**, 6457–6472.
30 *Anion Recognition in Supramolecular Chemistry*, ed. P. A. Gale and W. Dehaen, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, vol. 24.
31 T. W. Bell and N. M. Hext, *Chem. Soc. Rev.*, 2004, **33**, 589–598.
32 Y. Wang, Y. Wang, S. Sahu, A. A. Gallo and X.-D. Zhou, *Polymers*, 2023, **15**, 352.
33 I. A. Rather, S. A. Wagay and R. Ali, *Coord. Chem. Rev.*, 2020, **415**, 213327.
34 I. A. Rather, S. A. Wagay, M. S. Hasnain and R. Ali, *RSC Adv.*, 2019, **9**, 38309–38344.
35 M. Savastano, C. García-Gallarín, M. D. López de la Torre, C. Bazzicalupi, A. Bianchi and M. Melguizo, *Coord. Chem. Rev.*, 2019, **397**, 112–137.
36 M. Savastano, C. Bazzicalupi, C. García-Gallarín, C. Giorgi, M. D. López de la Torre, F. Pichierri, A. Bianchi and M. Melguizo, *Dalton Trans.*, 2018, **47**, 3329–3338.
37 M. Savastano, C. Bazzicalupi, C. Giorgi, P. Gratteri and A. Bianchi, *Molecules*, 2017, **22**, 816.
38 C. Bazzicalupi, A. Bianchi, C. Giorgi, P. Gratteri, P. Mariani and B. Valtancoli, *Dalton Trans.*, 2013, **42**, 12130.

39 S. A. Wagay, L. Khan and R. Ali, *Chem.–Asian J.*, 2023, **18**, e202201080.
40 I. A. Rather, S. A. Khan, R. Ali, T. A. Khan and R. Ali, *J. Mol. Struct.*, 2022, **367**, 120406.
41 S. A. Wagay, I. A. Rather and R. Ali, *Mater. Today: Proc.*, 2021, **36**, 657–678.
42 J. Černý and P. Hobza, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5291.
43 E. R. Johnson, S. Keinan, P. Mori-Sánchez, J. Contreras-García, A. J. Cohen and W. Yang, *J. Am. Chem. Soc.*, 2010, **132**, 6498–6506.
44 A. S. Novikov, *Polymers*, 2023, **15**, 1139.
45 C. Puzzarini, L. Spada, S. Alessandrini and V. Barone, *J. Phys.: Condens.Matter*, 2020, **32**, 343002.
46 M. Savastano, C. Cappanni, C. Bazzicalupi, C. Lofrumento and A. Bianchi, *Crystals*, 2023, **13**, 823.
47 E. Mulugeta, Q. He, D. Sareen, S.-J. Hong, J. H. Oh, V. M. Lynch, J. L. Sessler, S. K. Kim and C.-H. Lee, *Chem*, 2017, **3**, 1008–1020.
48 J. Yoo, M.-S. Kim, S.-J. Hong, J. L. Sessler and C.-H. Lee, *J. Org. Chem.*, 2009, **74**, 1065–1069.
49 I. A. Rather, F. A. Sofi, M. A. Bhat and R. Ali, *ACS Omega*, 2022, **7**, 15082–15089.
50 I. A. Rather, R. Ali and A. Ali, *Org. Chem. Front.*, 2022, **9**, 6416–6440.
51 I. A. Rather, S. A. Khan, R. Ali and T. A. Khan, *J. Mol. Liq.*, 2022, **367**, 120406.
52 A. Kim, R. Ali, S. H. Park, Y.-H. Kim and J. S. Park, *Chem. Commun.*, 2016, **52**, 11139–11142.
53 M. K. Deliomeroglu, V. M. Lynch and J. L. Sessler, *Chem. Sci.*, 2016, **7**, 3843–3850.
54 M. K. Deliomeroglu, V. M. Lynch and J. L. Sessler, *Chem. Commun.*, 2014, **50**, 11863–11866.
55 P. A. Gale, J. L. Sessler, V. Král and V. Lynch, *J. Am. Chem. Soc.*, 1996, **118**, 5140–5141.
56 C. Guo, S. Sun, Q. He, V. M. Lynch and J. L. Sessler, *Org. Lett.*, 2018, **20**, 5414–5417.
57 Y. Zhou and X. Bao, *Spectrochim. Acta, Part A*, 2019, **210**, 1–8.
58 R. Yi, X.-L. Liu, Z.-H. Tang, C. Huang, B.-X. Zhu and C. Zhu, *Chem. Pap.*, 2021, **75**, 4405–4411.
59 E. A. Katayev, N. V. Boev, V. N. Khrustalev, Y. A. Ustynyuk, I. G. Tananaev and J. L. Sessler, *J. Org. Chem.*, 2007, **72**, 2886–2896.
60 J. L. Sessler, V. Roznyatovskiy, G. D. Pantos, N. E. Borisova, M. D. Reshetova, V. M. Lynch, V. N. Khrustalev and Y. A. Ustynyuk, *Org. Lett.*, 2005, **7**, 5277–5280.
61 X. Zhang, Y. Shiraishi and T. Hirai, *Tetrahedron Lett.*, 2007, **48**, 8803–8806.
62 Z.-H. Fu, X. Han, Y. Shao, J. Fang, Z.-H. Zhang, Y.-W. Wang and Y. Peng, *Anal. Chem.*, 2017, **89**, 1937–1944.
63 D. Y. Lee, N. Singh, M. J. Kim and D. O. Jang, *Org. Lett.*, 2011, **13**, 3024–3027.
64 I. Hussain, N. B. Singh, A. Singh, H. Singh and S. C. Singh, *Biotechnol. Lett.*, 2016, **38**, 545–560.
65 H. J. Jung, N. Singh, D. Y. Lee and D. O. Jang, *Tetrahedron Lett.*, 2010, **51**, 3962–3965.
66 F. Ullah, T. A. Khan, J. Iltaf, S. Anwar, M. F. A. Khan, M. R. Khan, S. Ullah, M. Fayyaz ur Rehman, M. Mustaqeem, K. Kotwica-Mojzych and M. Mojzych, *Appl. Sci.*, 2022, **12**, 1102.
67 G. W. Gokel, W. M. Leevy and M. E. Weber, *Chem. Rev.*, 2004, **104**, 2723–2750.
68 V. Rüdiger, H.-J. Schneider, V. P. Solov'ev, V. P. Kazachenko and O. A. Raevsky, *Eur. J. Org Chem.*, 1999, **1999**, 1847–1856.
69 A. A. Saddik, M. Mohammed and H.-C. Lin, *J. Mater. Chem. B*, 2020, **8**, 9961–9970.
70 I. A. Rather and R. Ali, *Green Chem.*, 2021, **23**, 5849–5855.
71 P. C. A. Swamy, R. N. Priyanka and T. Pakkirisamy, *Dalton Trans.*, 2014, **43**, 4067.
72 M. Alešković, N. Basarić, K. Mlinarić-Majerski, K. Molčanov, B. Kojić-Prodić, M. K. Kesharwani and B. Ganguly, *Tetrahedron*, 2010, **66**, 1689–1698.
73 M. Alešković, N. Basarić, I. Halasz, X. Liang, W. Qin and K. Mlinarić-Majerski, *Tetrahedron*, 2013, **69**, 1725–1734.
74 I.-W. Park, J. Yoo, B. Kim, S. Adhikari, S. K. Kim, Y. Yeon, C. J. E. Haynes, J. L. Sutton, C. C. Tong, V. M. Lynch, J. L. Sessler, P. A. Gale and C.-H. Lee, *Chem.–Eur. J.*, 2012, **18**, 2514–2523.
75 G. Gil-Ramírez, E. C. Escudero-Adán, J. Benet-Buchholz and P. Ballester, *Angew. Chem., Int. Ed.*, 2008, **47**, 4114–4118.
76 S. K. Kim, H. G. Lee, G. V-Zfflciga, V. M. Lynch, C. Kim and J. L. Sessler, *Chem.–Eur. J.*, 2014, **20**, 11750–11759.
77 J. Yoo, I. Park, T. Y. Kim and C. H. Lee, *Bull. Korean Chem. Soc.*, 2010, **31**(3), 630–634.