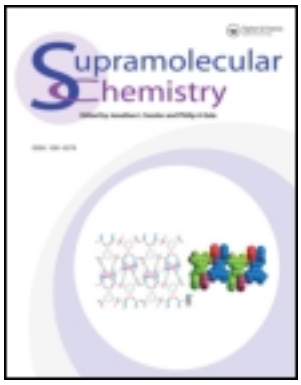

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Porphyrin-based receptors for selective ion bindings

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The functional porphyrin derivatives in biological systems provide various motivations for the design of biomimetic functional materials. Using the porphyrin moieties, we recently have designed several types of receptor molecules for the bindings of anionic and cationic species. By the combination of hydrogen-bonding motifs and porphyrins, selective bindings of anionic species have been achieved by means of hydrogen bonds and electrostatic interactions. In this study, we are going to briefly review the results of recent researches on porphyrin-based host system for selective ion bindings.

Keywords: porphyrin; host–guest chemistry; self-assembly; sensor

1. Introduction

Porphyrin is an aromatic macrocycle with expanded π-conjugation system. Owing to the expanded π-conjugation system, porphyrin derivatives exhibit strong absorption of visible light and have unique photo- and electro-functional properties (*1*, *2*). Furthermore, the photo- and electro-functional properties of porphyrin derivatives can be tuned by the coordination of metal ions into the porphyrin centre (*1*, *3*, *4*). Because of the symmetric architecture, porphyrins often utilised as the building blocks for the construction of supramolecular self-assemblies (*5*, *6*). In the biological system, porphyrin derivatives play many essential roles, such as oxygen transport (*7*), active site in enzyme (*8*) and light harvesting (*9*, *10*). The functional porphyrin derivatives in biological systems provide various motivations for the design of biomimetic functional materials. Using the porphyrin moieties, we recently have designed several types of receptor molecules for the bindings of anionic and cationic species (*11–16*). The designed porphyrin-based receptors exhibited unique properties, which have been utilised for various functional applications.

2. Porphyrin-based allosteric host systems

Allosterism is one the most fundamental regulation mechanisms in biological events (*17*, *18*). Proteins having multiple guest-binding sites often exhibit allosteric feedback mechanism. The oxygen bindings in haemoglobin would be one of the typical examples for allosteric guest bindings, in which the first oxygen binding causes a structural alteration of haemoglobin subunits to accelerate additional oxygen bindings (*7*). Designing such artificial allosteric systems is of great interest because not only of their crucial roles in biosystems but also for the design of artificial functional nanodevices. In this regard, we have designed several artificial receptors having positive allosterism (*11*).

As shown in Figure 1, we have designed porphyrin-based molecular tweezer (**1**) with biindole bridge. Because the NH protons in the indole moieties provide strong hydrogen-bonding sites to accommodate several anionic species (*19*), we have expected anions can bind to **1** by multiple hydrogen bonds. On the other hand, **1** can form stable complex with diamine guest because Lewis acidic zinc porphyrin is able to accept lone pair electron as axial ligand (*20*). To test the binding affinities of anion and diamine, Cl^- and 1,4-diazabicyclo[2.2.2]octane (DABCO) were titrated to **1** in tetrahydrofuran (THF). As a result, both Cl^- and DABCO exhibited strong binding affinities to **1**, where the association constants for Cl^- and DABCO were 4.93×10^4 and $2.02 \times 10^6\,M^{-1}$, respectively. In addition, ^1H NMR and ultraviolet–visible (UV–vis) absorption spectroscopic observation indicated the simultaneous bindings of both chloride and DABCO to **1**. Therefore, the binding affinities of Cl^- and DABCO to **1** were again estimated in the presence of 1 equiv. of DABCO and Cl^-, respectively. Interestingly, the binding affinities of both Cl^- and DABCO were greatly enhanced by the existence of the other guest, indicating that Cl^- and DABCO have strong heterotropic positive allosterism to each other upon the binding to **1**. The strong positive allosterism between Cl^- and DABCO can be explained as illustrated in Figure 2. The most stable *trans*-conformation of **1** can be changed to the *cis*-conformation by the initial guest bindings to enhance binding affinities of the second guest bindings.

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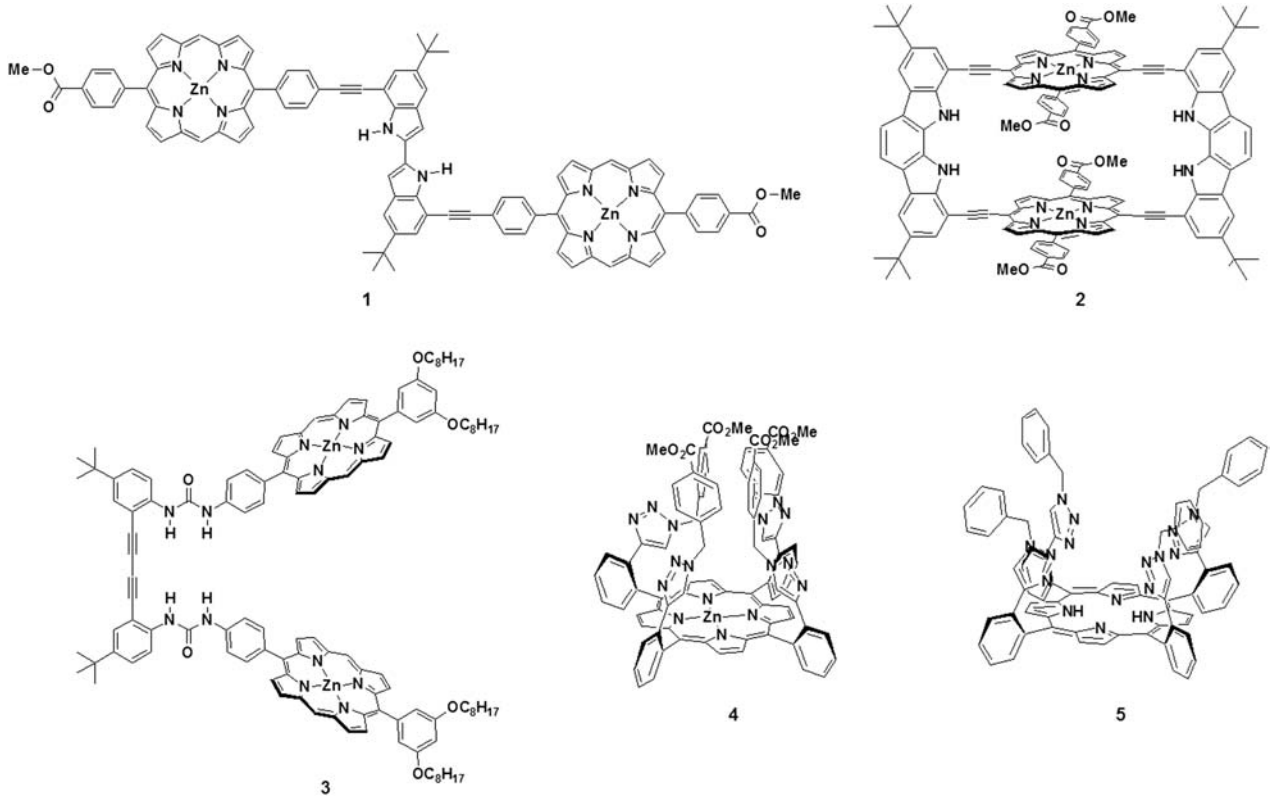

Figure 1. Various porphyrin-based receptors for ion bindings.

As another allosteric host system, we have developed indolocarbazole-bridged macrocyclic porphyrin dimer (**2**) (Figure 1) (*12*). The UV–vis titration study indicated that **2** forms 1:2 host–guest complexes with various anionic guests. Very importantly, the binding isotherms of $CH_3CO_2^-$, F^- and N_3^- to **2** were obviously sigmoidal curves, indicating the positive homotropic allosterism. When the anions were added to **2**, the structural alternation can be taken place to accommodate anionic guest (Figure 3). Because of the structural rigidity of porphyrin

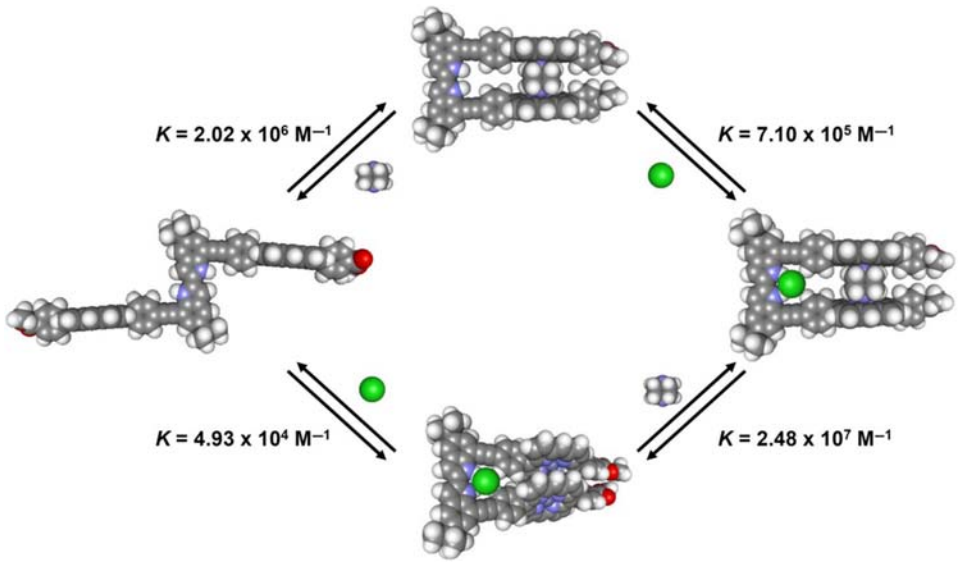

Figure 2. Energy-minimised molecular models of **1** and its host–guest complexes (*11*). Reproduced by permission of Wiley-VCH.

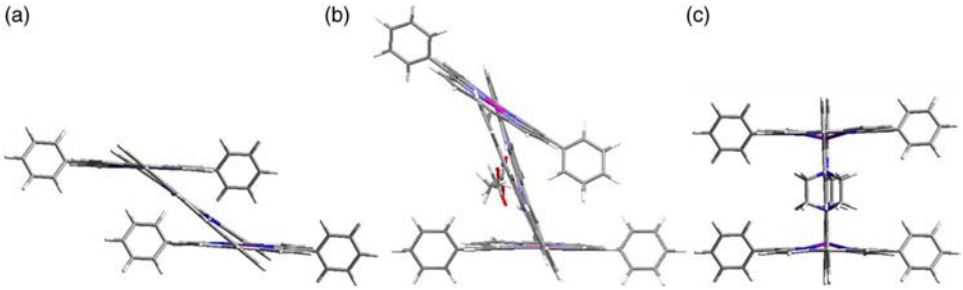

Figure 3. The optimised structures for (a) **2**, (b) **2** ⊃ acetate and (c) **2** ⊃ DABCO (*12*). Reproduced by permission of The Royal Society of Chemistry.

and indolocarbazole, the only rotatable bond in **2** would be ethynyl linkages between porphyrin and indolocarbazole units. Therefore, the angle between porphyrin and indolocarbazole units can be changed by the first anionic guest binding to **2**. On the other hand, when the 1 equiv. of DABCO was added to **2**, the homotropic allostericity of anionic guest bindings was greatly decreased. When the DABCO was bound to **2**, the dihedral angle between porphyrin and indolocarbazole units would eventually become perpendicular. Therefore, the structural alternation of **2** by anion bindings cannot be taken place. In summary, DABCO successfully worked as a heterotopic modulator for the allosteric anion binding to the host. The present system is, therefore, an excellent biomimetic model having homotropic allosterism with an inhibitory control mechanism.

3. Porphyrin-based molecular tweezer for chiral sensing

Recently, we have designed a new type of molecular tweezer (**3**) for the determination of absolute stereo configuration of chiral carboxylates (Figure 1) (*13*). The determination of absolute stereo configuration is significantly important topic in chemistry because many bioactive molecules are only effective when they have a specific stereo configuration (*21*). Several porphyrin tweezers have been developed as probes for absolute stereochemical determination based on exciton-coupled circular dichroism (ECCD), which is a CD signal induced by a chiral twist of the two porphyrin units due to the binding of chiral guest to porphyrin-based molecular tweezer (*22*). The ECCD method is a powerful tool but still has a severe limitation that precludes its current use in high-throughput screens or other real-time analyses. For example, tedious derivatisation is required for substrates bearing only a single ligation site (*23*). And also, a large excess of guest molecules is often needed to furnish a reliable CD signal due to their weak binding affinities. To overcome above drawbacks, two urea groups were introduced into porphyrin-based molecular tweezer as the remote guest-binding sites, which provided significantly high-binding affinity to chiral carboxylate without derivatisation. Figure 4 shows CD spectra of **3** in CH_2Cl_2 in the presence of 3 equiv. Boc-L-Ala (BLA), Boc-D-Ala (BDA) with or without 1,12-diaminododecane (DAD). When the chiral carboxylates were added to **3**, only weak CD signals were appeared. However, great signal amplification has been achieved by the addition of DAD, which binds to inner cavity of the two porphyrin units. Similar signal amplifications by DAD binding were observed for many other chiral carboxylates. The weak ECCD signal of **3** induced by carboxylate bindings and

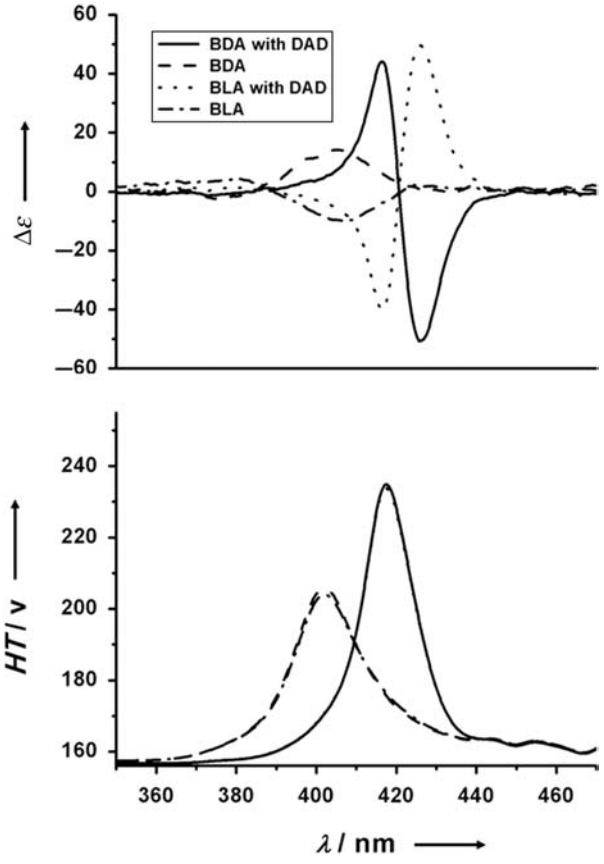

Figure 4. CD spectra of **3** in CH_2Cl_2 in the presence of 3 equiv. BLA, BDA with or without DAD (*13*). Reproduced by permission of Wiley-VCH.

strong signal amplification can be explained as illustrated in Figure 5. Without guest binding, **3** can form both *cis*- and *trans*-conformation. By the chiral carboxylate inclusion, **3** adopts *cis*-conformation due to the formation of multiple hydrogen bonds. The two urea groups would be twisted into chiral manner to minimise the steric repulsion. In this process, the direction of chiral twist would be dependent on the chirality of amino acid derivatives. Owing to the chiral twist of urea groups, **3** should exhibit ECCD signals. However, **3** exhibits only weak CD signals due to the formation of slipped-cofacial structure of porphyrin units. In contrast, the chiral distortion of urea groups can be transferred to two porphyrin units by the insertion of DAD between two porphyrin units. Therefore, the strong signals amplification can be observable by the addition of DAD to the chiral carboxylate complex of **3**.

4. Picket type porphyrin with triazole groups for anion bindings

A new picket type porphyrin-based host compound (**4**), tetraphenyl zinc porphyrin that contains four triazole groups at the *ortho*-position of each phenyl group, has been synthesised (Figure 1) (*14*). Owing to the considerable interest for artificial anion-binding receptors, various receptors with multiple hydrogen-binding donors have been designed. For example, several indole- or pyrrole-based macrocyles and foldamers have exhibited strong binding affinities to anionic guests through multiple N—H···X hydrogen bonds (*11*, *12*, *19*, *24*). In addition to N—H···X hydrogen bonding, C—H···X is also very important in the recognition of biological anions (*25*). The Flood's macrocylic triazolophanes would be a typical example of C—H···X hydrogen bonding mediated host for anionic guest binding, which exhibited unexpectedly high-binding affinity to Cl ($K = 1.1 \times 10^7\ M^1$ in CH_2Cl_2) due to the shape-persistent nature of host compound (*26*). Based on the above information, we expected that **4** can accommodate anionic guest owing to the multiple C—H···X hydrogen-bonding donors. Interestingly, **4** exhibited extremely high halide-binding affinities without shape-persistent macrocyclic structure of triazole groups, where the association constants for Cl^-, Br^- and I^- were $>10^8$, 1.79×10^7 and $1.84 \times 10^5\ M^{-1}$, respectively. The host–guest complex formation between **4** and halides has been directly confirmed by MALDI-TOF-MS analysis (Figure 6) using negative ionisation mode. Upon the ^1H NMR study in DMSO, the triazole, benzyl and phenylene proton signals were shifted upfield by the addition of halides, implies that the triazole protons in **4** are allocated very closely to the porphyrin ring and are directed towards the binding pocket over the porphyrin ring. The UV–vis absorption spectra exhibited that both Soret and Q band absorptions of **4** underwent a strong red shift due to the addition of halides. The UV–vis absorption changes and the result of competitive titration using 4-tert-butylpyridine indicated that the cooperative effects of axial coordination and C—H···X hydrogen bond interactions resulted in the strong binding affinity of **4** to halides. The degree of red shift by guest addition was greatly dependent on guest species. Such unique aspect has recently been utilised to the determination of impurity in commercial acetonitrile (MeCN). Although MeCN is a relatively inert solvent, a small quantity of impurities often causes serious interferences in many applications. Because commercial MeCN contains considerable amounts of impurities, various purification methods have been developed to obtain high-quality solvents. In some cases, MeCN includes highly toxic cyanide ions as a contaminant. As aforementioned, the absorption spectrum of **4** exhibited a red shift by the axial coordination of anions or amines, where the degree of the bathochromic shift was clearly dependent on the electron-donating ability of guests (*15*). Figure 7 shows guest-dependent absorption spectra of **4** in purified MeCN. Because the absorption maximum of **4** was varied by the coordination of guest species, the absorption spectra of **4** in six commercial MeCN were measured to confirm the existence of impurity. From the absorption spectra, we could find out that three commercial MeCN include cyanide. Moreover, sub-ppm level cyanide contamination in commercial MeCN has been confirmed by spectroscopic titration or colorimetric method.

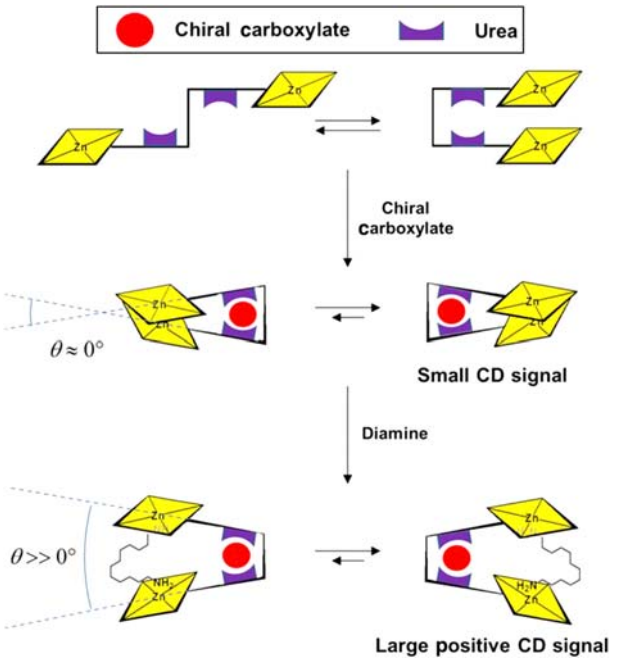

Figure 5. Proposed mechanism of CD enhancement of **3** by guest bindings (*13*). Reproduced by permission of Wiley-VCH.

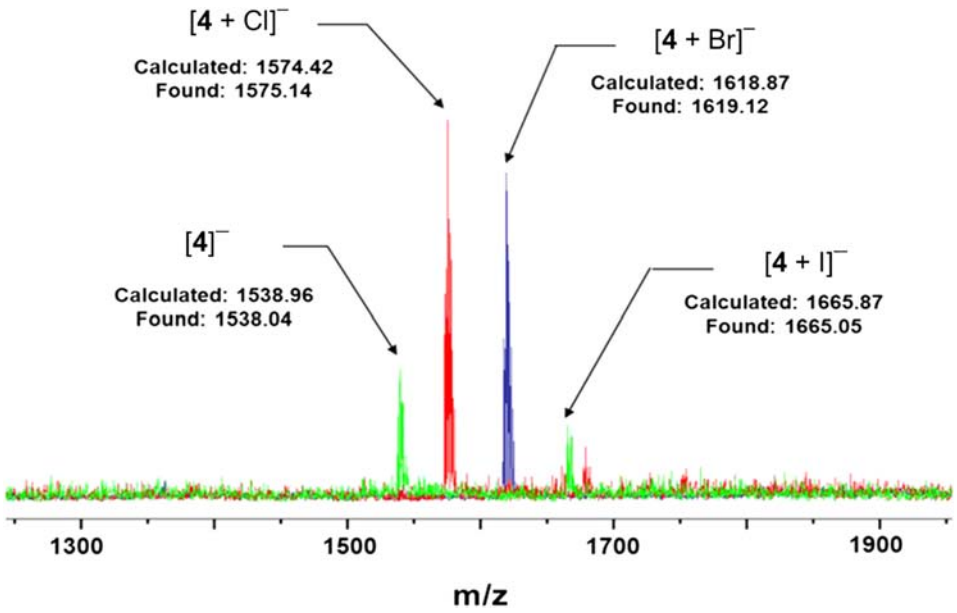

Figure 6. MALDI-TOF-MS spectra of **4** with halides (*14*). Reproduced by permission of Wiley-VCH.

5. Picket type porphyrin with triazoles as host for lanthanide

The triazole-bearing picket type porphyrin (**5**) has been utilised as the ligand for lanthanide coordination (Figure 1) (*16*). Organic lanthanide complexes have great potential for the application in light-converting optical materials, light-emitting layers in electroluminescent devices, contrast agents for MRI and luminescent probes for biological evaluations (*27*). For the design of lanthanide-based photoluminescent materials, the design of organic ligand molecule is greatly important issue (*28*). Porphyrin derivatives have been extensively investigated as a multidentate ligand for lanthanide. Although several monoporphyrinate lanthanide complexes (MPLCs) have been designed, most of them include ancillary ligand coordination, and lanthanide with large ionic radius results in unstable complexes (*29*). Because the triazole nitrogen can provide metal coordination site, we expect that **5** can form stable complexes by lanthanide coordination. In fact, **5** formed very stable coordination complexes with Eu^{3+}, Tb^{3+} and Er^{3+}, which have been directly confirmed by MALDI-TOF-MS analysis (Figure 8). The electronic absorption changes also indicated the formation of lanthanide complexes. After the coordination of lanthanide to **5**, the Soret absorption band slightly red shifted with the reduced number of Q bands due to an increase in symmetry by metal coordination into the porphyrin ring (Figure 9).

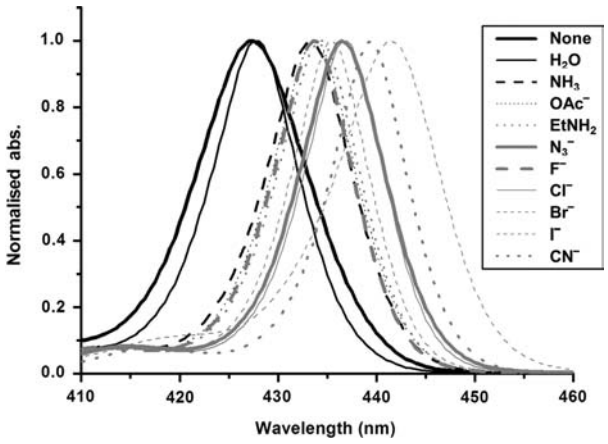

Figure 7. Guest-dependent spectral shift of **4** in purified MeCN (*15*). Reproduced by permission of The Royal Society of Chemistry.

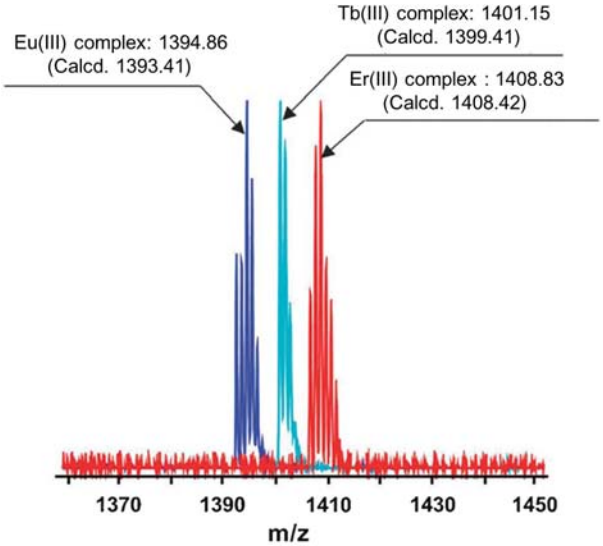

Figure 8. MALDI-TOF-MS spectra of MPLCs (*16*). Reproduced by permission of The Royal Society of Chemistry.

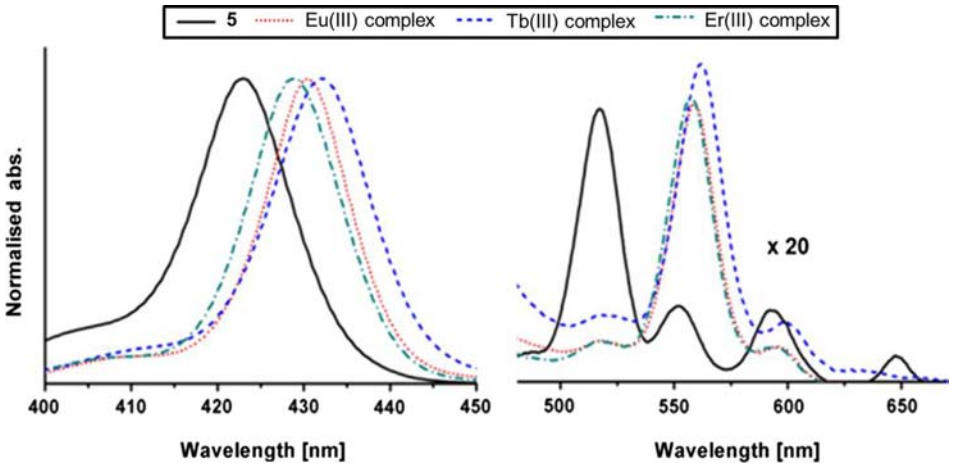

Figure 9. UV–vis absorption spectra of **5** and MPLCs (*16*). Reproduced by permission of The Royal Society of Chemistry.

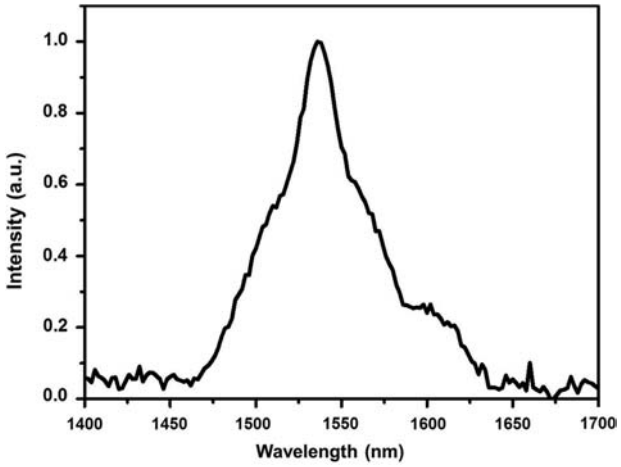

Figure 10. Near IR emission from Er(III) complex of **5** (*16*). Reproduced by permission of The Royal Society of Chemistry.

Also, **5** exhibited reduced fluorescence emission in visible range by the lanthanide coordination. Very importantly, we could observe the characteristic near infrared (NIR) emission of Er^{3+} complex, indicating that **5** successfully works as the photosensitising organic ligand for lanthanide ions (Figure 10). Although only three kinds of lanthanide ions have been utilised for the formation of MPLCs with **5**, we expect that this triazole-bearing porphyrin is an excellent ligand for a wide range of lanthanide coordination. Further investigation would give valuable information for the application of lanthanide complex in materials chemistry.

6. Conclusion

In this study, we have briefly reviewed our recent researches on porphyrin-based host compounds for ion bindings. By the combination of hydrogen-bonding motifs with porphyrin derivatives, we have synthesised various types of porphyrin-based host compounds having unique properties, such as allosteric effect and molecular recognition. Such unique properties can be utilised for the signal amplification and for the design of photofunctional materials.

Acknowledgements

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