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Re(I) bridged porphyrin dyads, triads and tetrads

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Abstract. Porphyrin rings containing two *meso-pyridyl* groups either in *cis* or *trans* fashion can be used to construct Re(I) bridged multiporphyrin assemblies. The *cis*-dipyridyl porphyrins with various porphyrin cores such as N_4, N_3O, N_3S, N_2S_2 have been used to react with $Re(CO)_5Cl$ in THF at refluxing temperature and constructed planar Re(I) bridged porphyrin dyads containing either one type of porphyrin subunit or two types of porphyrin subunits. The *trans*-dipyridyl porphyrins have been used to construct Re(I) bridged porphyrin squares. The porphyrin dyads have been explored for singlet–singlet energy transfer studies and porphyrin squares have been used for catalysis, chemical sensing, molecular sieving and photocurrent production studies. An overview of synthesis of Re(I) bridged porphyrin dyads, triads and tetrads and their interesting photophysical properties are highlighted in this paper.

Keywords. Re(I) bridged porphyrin arrays; core-modified porphyrins; fluorescence properties; energy transfer.

1. Introduction

The importance of multichlorin assemblies in photosynthetic reaction centers and light-harvesting antenna complexes has inspired considerable interest in the synthesis of multiporphyrin assemblies such as dyads, triads, tetrads, pentads and higher oligomers.[1] Besides mimicking biological systems, the multiporphyrin assemblies are also essential for the construction of functional systems such as molecular switches, optoelectronic gates, fluorescence quenching sensors, photonic wires, and molecular elements for information storage essential for the miniaturization of electronic componentry and technology.[2] Three-dimensional metalloporphyrin oligomers are also actively investigated as host molecules for homogeneous catalysis and selective molecular recognition that can result from the specific geometry of cavities defined by porphyrin planes.[3] Interestingly, some multiporphyrin assemblies have been tested for photodynamic therapy of tumors and DNA cleavage.[4] Design strategies to develop solid-state multichromophore arrays of defined rigidity, dimensionality, porosity, and selectivity are also a part of active research.[5]

There are two approaches to synthesize multiporphyrin assemblies: covalent and non-covalent. The covalently linked multiporphyrin assemblies[6] have been investigated extensively by employing several synthetic strategies and synthesized a wide variety of porphyrin arrays containing two or more porphyrin subunits connected by variety of bridging groups such as phenyls, biphenyls, aromatic heterocycles, alkenes, alkynes and directly connected porphyrin assemblies without using any bridging groups. However, the covalent synthetic strategies to porphyrin arrays have generally proved quite limiting. The covalent synthetic strategies requires many sequential steps; involves separation of statistical mixtures and extensive chromatographic purification resulting in a low product yield. Non-covalent approaches[7] such as hydrogen bonding, metal-ligand coordination and their combination has emerged as a viable alternative to covalent synthesis in the construction of large multi-porphyrin architectures. To a large extent, the majority of the non-covalent self-assembling porphyrin arrays are based on metal–ligand interactions and hydroxyl or N-donor ligands such as imidazole, pyrazole, amine, pyridine usually at the *meso* positions play a key role in this kind of self-assembled multi-porphyrin assemblies.[8] In metal mediated self-assembly approach,[8] the porphyrins and metalloporphyrins can be exploited essentially in two ways as modules: (i) metalloporphyrins can be acceptor building blocks provided that the metal atom inside the porphyrin core has atleast one axial site available for coordination (chart 1). For example, the zinc ion inside zinc-porphyrin prefers to adopt a five-coordinate square-pyramidal geometry and has a good affinity for

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*For correspondence

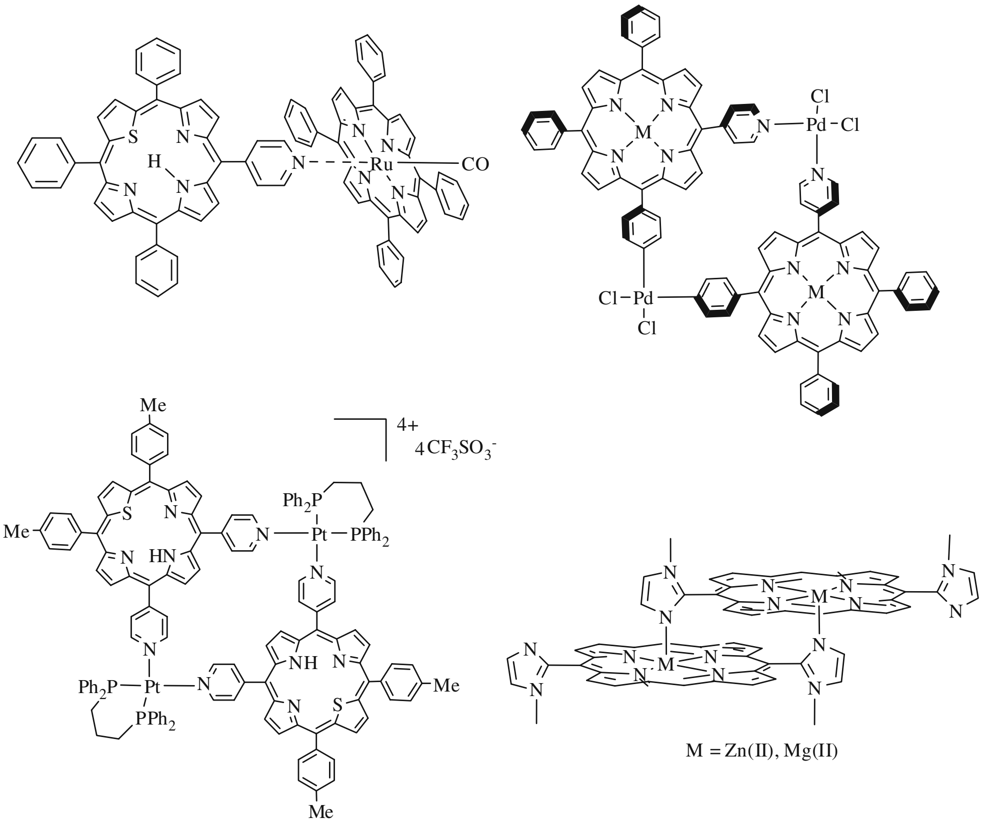
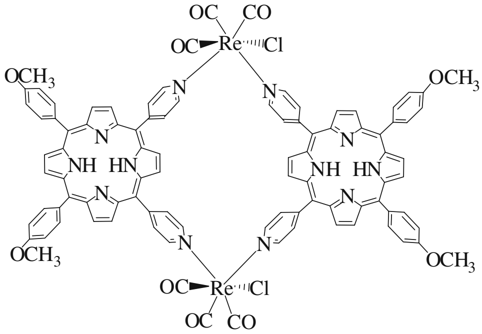


Chart 1. Selected examples of metal bridged porphyrin dyads.



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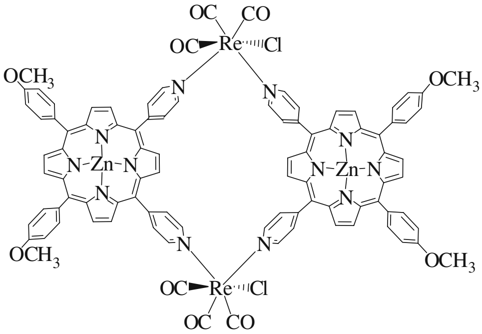

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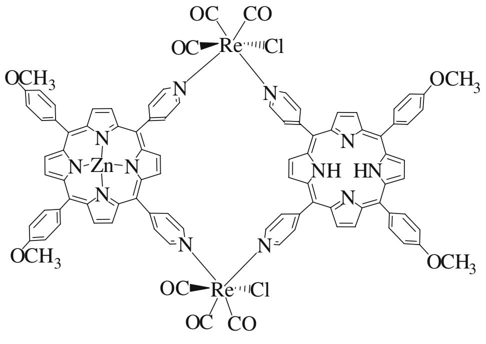

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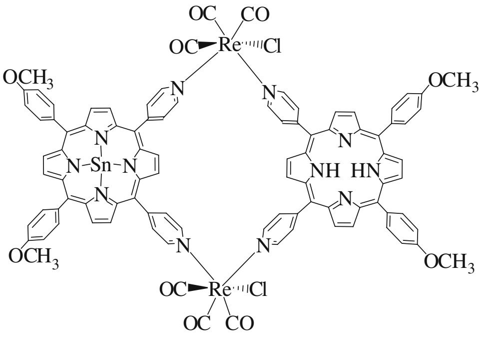

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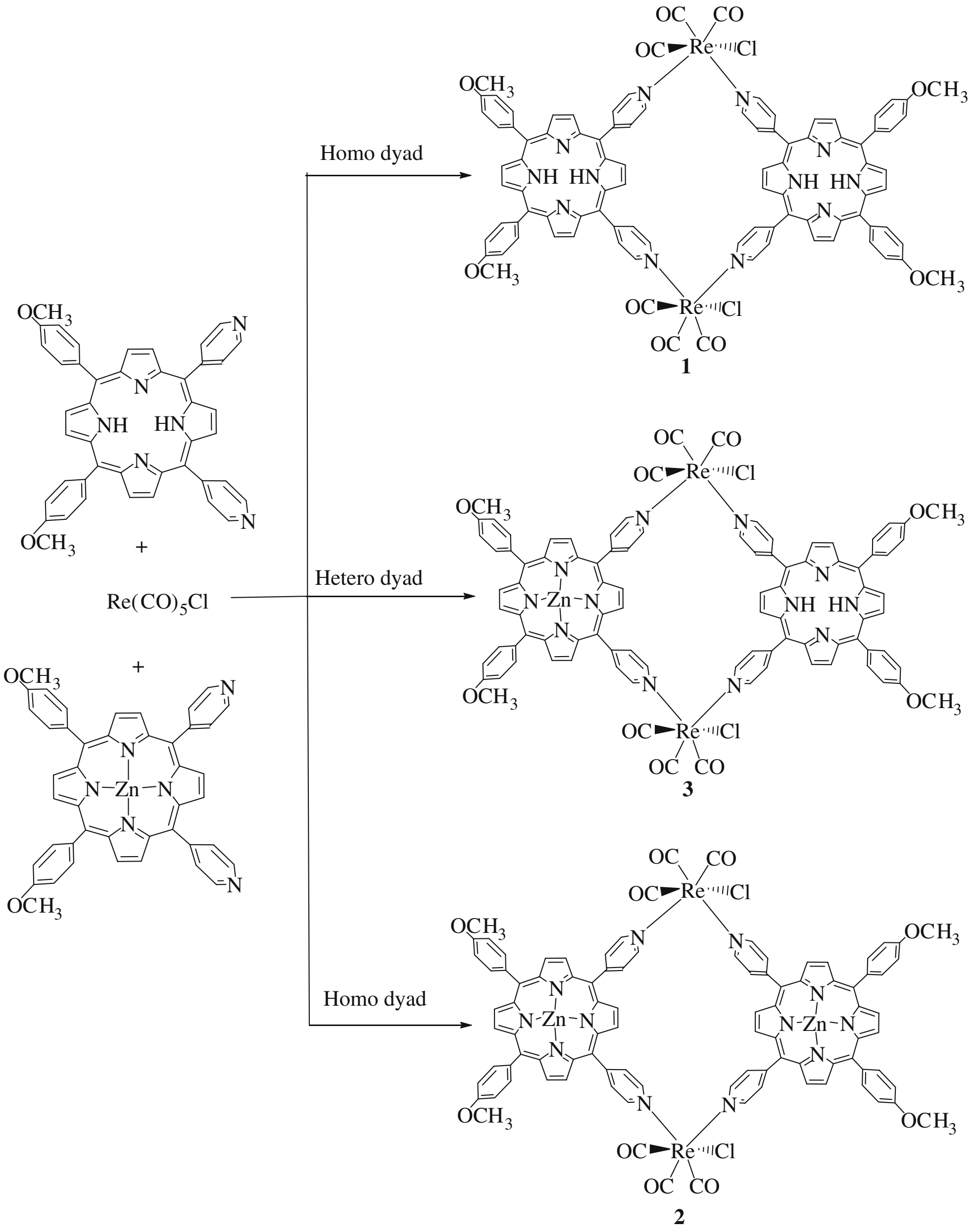
Chart 2. Re(I) bridged homo and hetero porphyrin dyads.



Scheme 1. Synthesis of porphyrin dyads **1–3**.

nitrogen donor ligands. Many metalloporphyrin assemblies obtained both in solution and as crystalline materials are based on the zinc-porphyrin-N-heterocycle (pyridine, imidazole) interaction which is intrinsically weak and relatively labile.[9] The stronger and more inert bonds to N-heterocycles are obtained with Ru^{II}(CO)-, Os^{II}(CO)-, or Rh^{III}-(halide)-porphyrin interaction.[7] Also in such cases, only one axial coordination site can be exploited for supramolecular construction because, even though the metal atom is six-coordinate, the carbonyl or halide ligands are very tightly bound and not easily displaced. On the other hand, Sn^{IV}-porphyrins adopt a six coordinate geometry, prefer oxygen donor ligands, and exchange the axial ligands rather slowly.[10] (ii) porphyrins can behave as donor building blocks, provided that they have ligands appended to the periphery that can suitably coordinate to metal centers (chart 1). Most of the examples reported in the literature were based on porphyrins elaborately decorated with covalently attached hydroxyl or N-donor ligands usually at the *meso* positions. The *meso*-pyridyl/phenyl porphyrins are proved to be versatile building blocks[7] since the *meso*-pyridyl porphyrins provide geometrically well-defined connection to as many as four metal

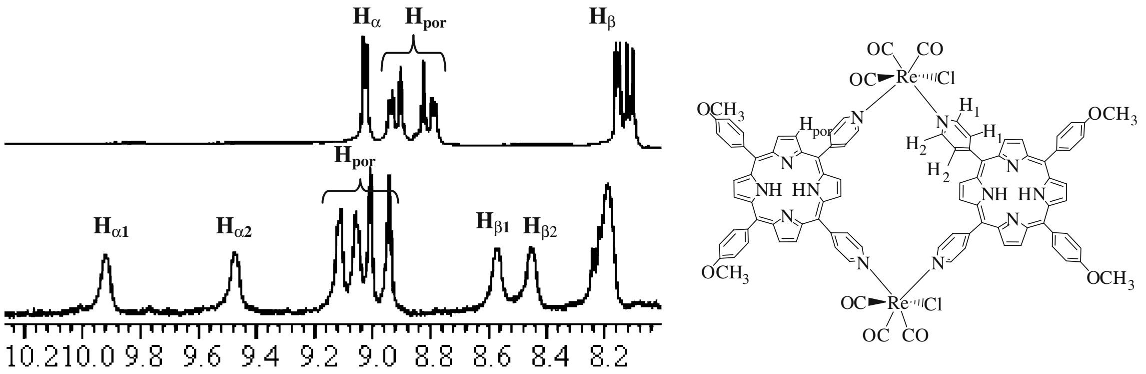


Figure 1. Comparison of ^{1}H NMR spectra of *cis meso*-pyridylporphyrin (*Cis* DPyP) and its homo dyad **1**.

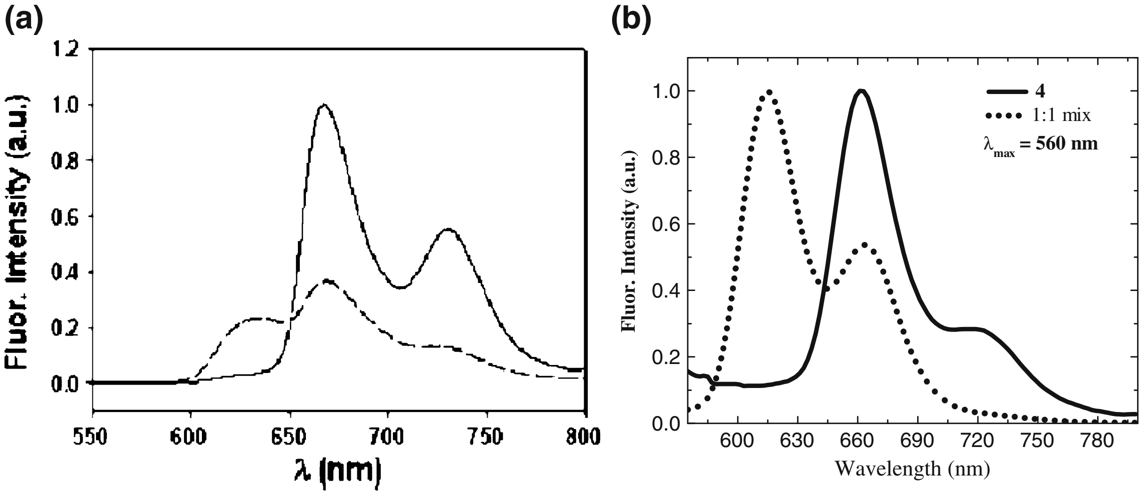


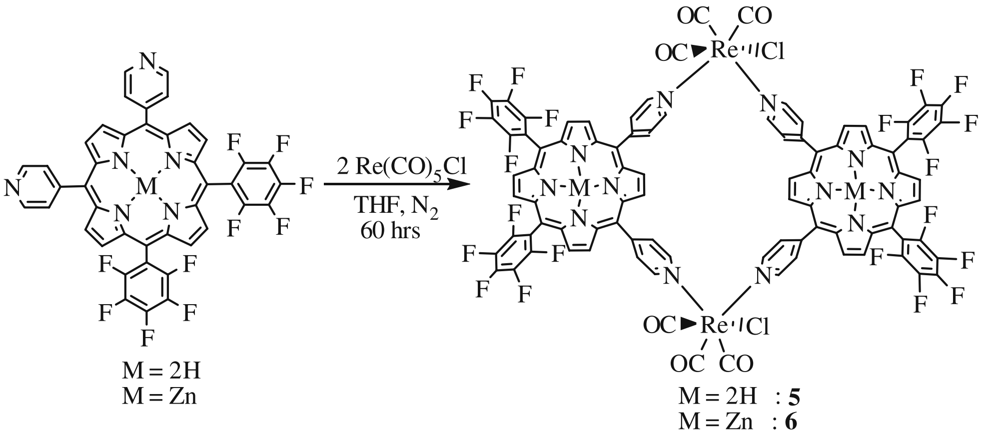
Figure 2. (**a**) Fluorescence spectra recorded in THF of **3** (—) and an equimolar of **1** and **2** (---). λ_{ex} = 450 nm, where A = 0.20 for both solutions. (**b**) Comparison of emission spectra of dyad **4** with 1:1 mixture of its porphyrin monomers recorded at λ_{ex} = 560 nm in dichloromethane.

centers by coordination of the pendant *meso*-pyridyl groups. There are several examples in the literature on *meso*-pyridyl porphyrinbased assemblies[7] where the pyridyl group coordinates to a metal centre that is present in the core of the porphyrin molecules (chart 1). The most widely used metals are Zn(II), Ru(II) and Os(II) although other metals such as Mg, Fe, Mn, etc. have also been used. Metals like Pd(II) and Pt(II) metal complexes have been used extensively to construct several types of metal mediated porphyrin architectures containing cavities with precise size and shape.[11] The building of such metal mediated assemblies is very interesting from the synthetic point of view but the possibility of studying properties like energy transfer at singlet state suffer a setback because of the presence of the heavy metals like Ru(II), Pd(II), Pt(II), etc. which quenches the emission by heavy atom effect. The recent studies showed that metal mediated porphyrin assemblies constructed using Re(I) ions are significantly fluorescent[12] and useful to study the porphyrin–porphyrin energy transfer at singlet state. In this paper an attempt has been made to give an overview of Re(I) bridged porphyrin dyads, triads and tetrads including discussion on their energy transfer properties.

2. Results and discussion

2.1 *Re(I) bridged porphyrin dyads*

Hupp and co-workers[13] first reported the synthesis of Re(I) bridged porphyrin homo dyads containing two same type of porphyrin subunits and hetero dyads containing one metal derivative and one free base



Scheme 2. Synthesis of Re(I) bridged porphyrin dyads **5** and **6**.

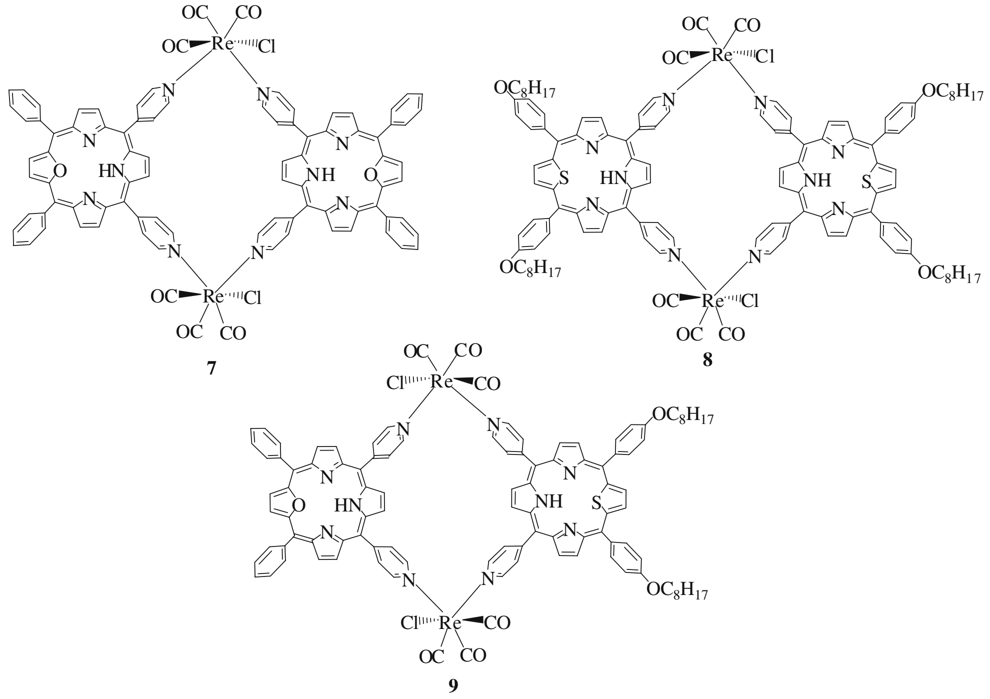
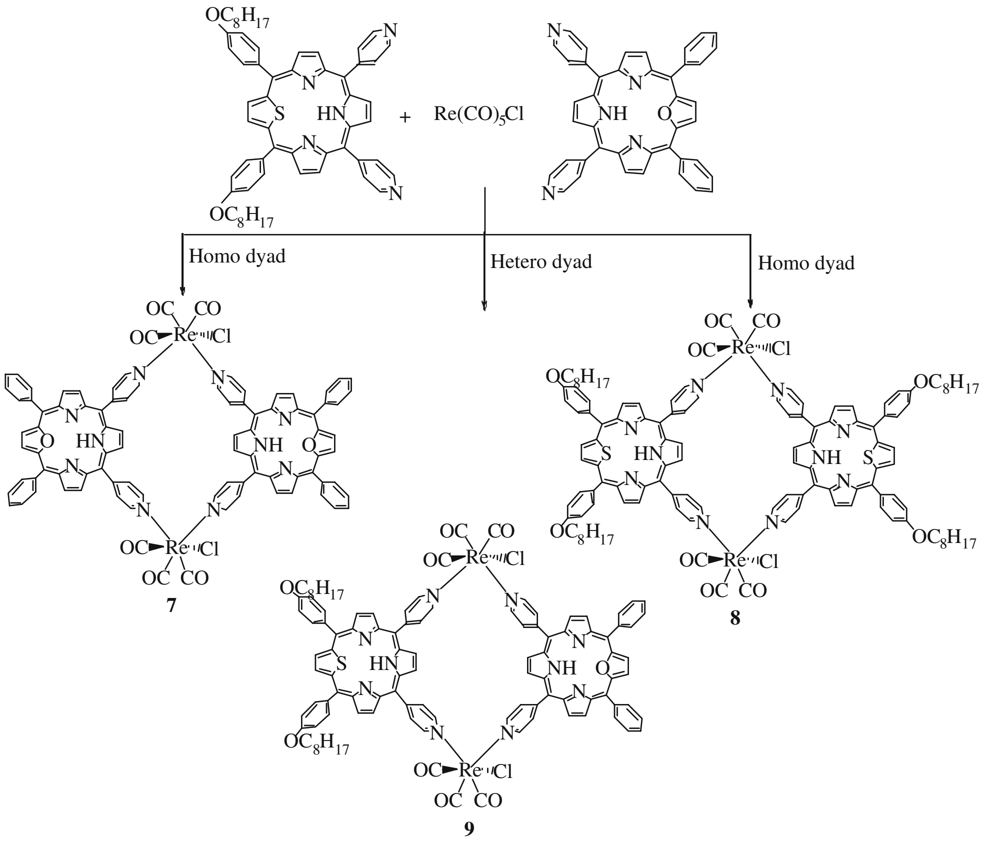


Chart 3. Re(I) bridged porphyrin dyads **7–9** containing heteroporphyrin subunits.

porphyrin subunits (chart 2). The homo dyads containing two N_4 porphyrin subunits **1** or two Zn(II) derivatives of N_4 porphyrins **2** were prepared by reacting stoichiometric amounts of *cis*-dipyridyl porphyrin 5, 10-*bis*(4-methoxyphenyl)-15,20-(4-pyridyl) porphyrin (*cis*-DPyN_4P) or its Zn(II) derivative (*cis*-ZnDPyN_4P) with $Re(CO)_5Cl$ in THF at refluxing temperature followed by column chromatographic purification gave dyads **1** and **2** in ∼75% yield. The hetero dyad **3** containing ZnN_4 and N_4 porphyrin subunits was prepared by reacting 0.5 equivalent each of *cis*-DPyN_4P and *cis*-ZnDPyN_4P with 1 equivalent of $Re(CO)_5Cl$ in THF under same reaction conditions (scheme 1). The reaction gave mixture of three dyads **1**, **2** and **3** which were separated by preparative thin-layer chromatography and obtained dyad **3** in decent yield. The reaction was expected to give a statistical mixture of *cis* and *trans* isomers of dyad **3** with respect to the chloro ligand orientation. Both isomers exhibit identical spectral features but they differ slightly in their ground state dipole moments. Hupp and co-workers[12,13] separated these isomers using preparative TLC and



Scheme 3. Synthesis of Re(I) bridged porphyrin dyads **7–9** containing heteroporphyrin subunits.

studied their transient direct current photoconductivity (TDCP). The TDCP approach reports changes in dipole moment, μ, upon photoexcitation. This technique measures the quantity: μ^2 (ground state) – μ^2 (excited state). The ground state dipole moment for the *trans* isomer is zero by symmetry but greater than zero for the *cis* isomer. Photo excitation causes identical changes in dipole moment μ (ground state) – μ (excited state) for the two isomers but different changes in μ^2 (ground state) – μ^2 (excited state). Their study showed that the *cis* isomer which elutes first was having largest TDCP value of 0.3 D. The dyads formation was clearly confirmed by NMR, mass, absorption and emission spectroscopic techniques. The comparison of ^{1}H NMR spectra of homo dyad **1** along with its porphyrin monomer *cis*-DPyN$_4$P is shown in figure 1. The ^{1}H NMR spectrum of dyad **1** was more complex than porphyrin monomer. Specially, the dyad formation was clearly reflected in the *meso*-pyridyl α and β protons which are involved in the coordination with Re(I) ions (figure 1). The number of α and β proton signals were doubled in dyad compared to its monomer. In dyads, the α protons were significantly downfield shifted compared to β-protons (figure 1). The dyads formation was also resulted in 8–10 nm red shift in absorption and emission maxima compared to monomeric pyridyl porphyrin because of the coordination of the pyridyl groups to the Re(I) metal centers. However, the interesting feature of the dyads are that

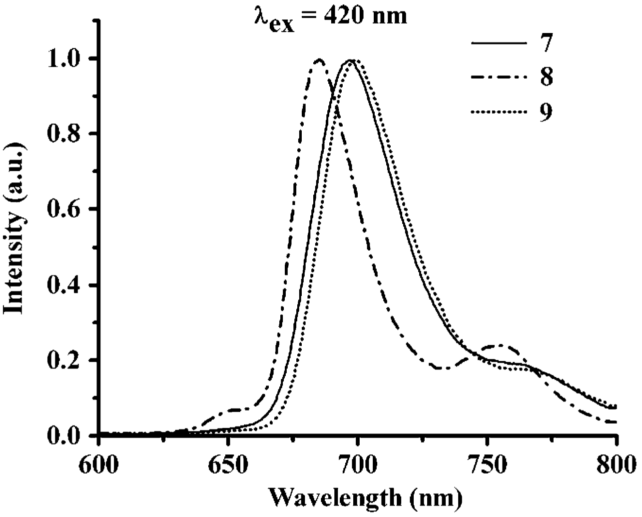


Figure 3. Fluorescence spectra of dyads **7–9** recorded at $\lambda_{ex} = 420$ nm in toluene.

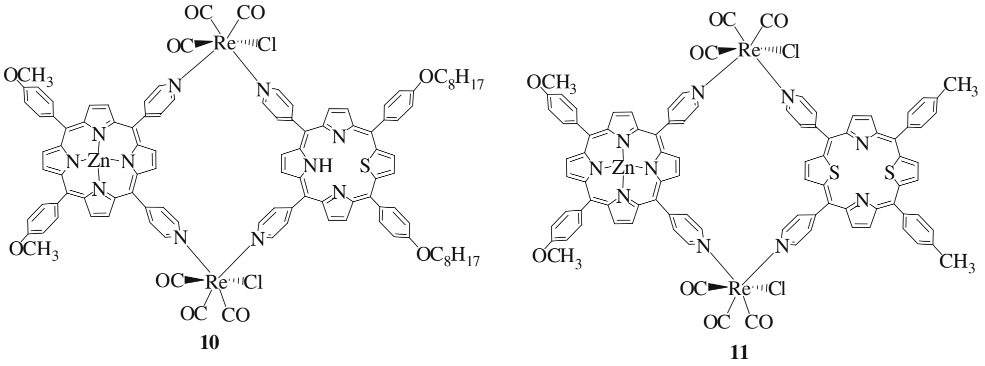


Chart 4. Re(I) bridged hetero dyads **10** and **11** containing two different porphyrin subunits.

they are significantly fluorescent despite incorporation of rhenium ions into assembly. Although the quantum yields of homo dyads were decreased by 75% due to the presence of Re(I) centers, these dyads are enough fluorescent for photophysical studies. Specially, the dyad **3** containing Zn(II) porphyrin and free base porphyrin was explored for energy transfer studies at singlet state. The fluorescence spectra of dyad **3** and equimolar mixture of dyads **1** and **2** recorded on excitation at Soret band is shown in figure 2a. As clear from figure 2a, in dyad **3**, the emission of ZnN_4 porphyrin was quenched significantly and emission was a) b) occurred mainly from free base porphyrin unit unlike equimolar mixture of homo dyads **1** and **2** in which the emission was occurred from both the dyads supporting an efficient energy transfer from ZnN_4 porphyrin subunit to N_4 porphyrin subunit in dyad **3**. Similar observations were made in our recently prepared[14] dyad **4** containing SnN_4 porphyrin and N_4 porphyrin subunits (chart 2). The fluorescence spectra of **4** along with 1:1 mixture of its corresponding porphyrin monomers recorded using excitation wavelength of 560 nm is shown in figure 2b. The dyad **4** on excitation at 560 nm where SnN_4 porphyrin subunit absorbs strongly, the emission from SnN_4 porphyrin was quenched significantly and main emission was noted from N_4 porphyrin subunit. However, in 1:1 mixture of its porphyrin monomers, on excitation at 560 nm, the emission was noted exclusively from SnN_4 porphyrin. These observations support that in dyad **4**, an efficient energy transfer occurs from SnN_4 porphyrin subunit to N_4 porphyrin subunit on selective excitation at 560 nm where SnN_4 porphyrin subunit absorbs strongly. Hupp and co-workers[15] also prepared Re(I) bridged two homo dyads **5** and **6** containing strongly electron withdrawing pentafluorophenyl groups at *meso*-positions (scheme 2). Spectroscopic and electrochemical properties indicated that the dyads remain planar and the presence of strong electron withdrawing groups at *meso* positions did not interfere with the geometry of the dyads.

Santosh and Ravikanth used the same strategy[16] to synthesize porphyrin dyads containing two free base heteroporphyrin subunits. Heteroporphyrins or core-modified porphyrins resulted from the replacement of one or two inner nitrogen atoms with heteroatoms such as O, S, Se and Te possess interesting electronic and photophysical properties.[17] Specially, the singlet state energy levels of heteroporphyrins can be fine tuned by replacing one or two inner nitrogens with appropriate heteroatoms. Thus, dyads containing two different porphyrin subunits in free base form whose singlet state energy levels are arranged in cascade manner can be used to study singlet–singlet energy transfer. We synthesized several such covalently linked porphyrin dyads and higher oligomers containing two or more different porphyrin subunits and demonstrated energy transfer from one porphyrin subunit to another.[17,18] Since

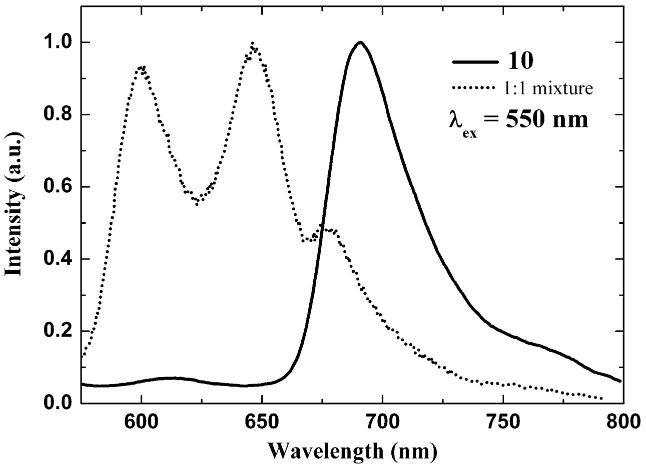
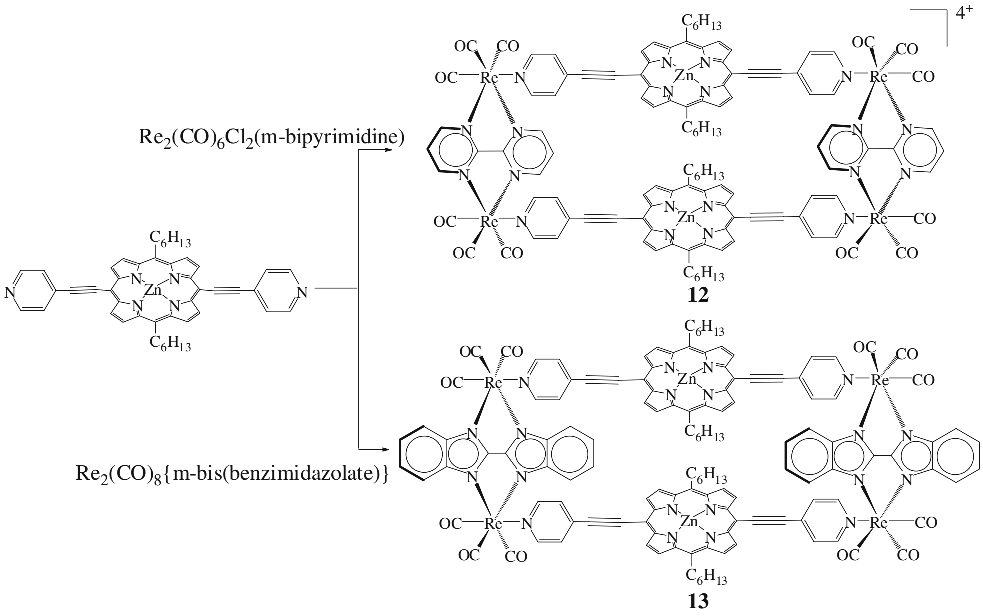


Figure 4. Comparison of fluorescence spectra of hetero dyad **10** along with its corresponding 1:1 mixture of porphyrin monomers recorded at $\lambda_{ex} = 550$ nm in toluene.



Scheme 4. Synthesis of Re(I) bridged porphyrin rectangles.

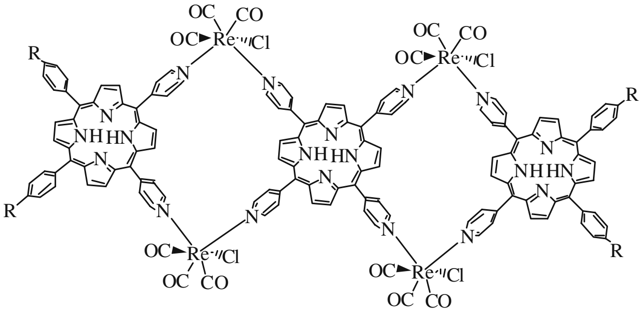
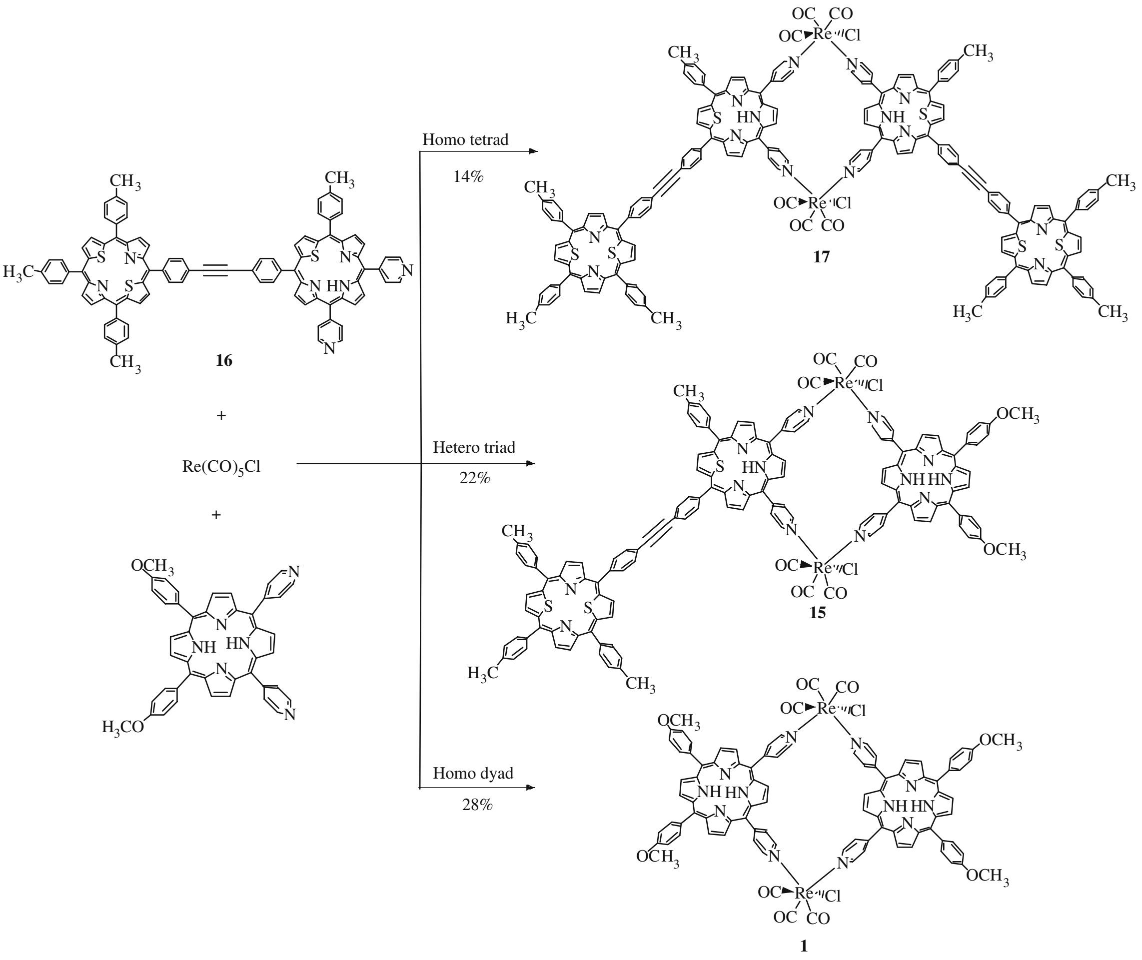


Chart 5. Proposed Re(I) bridged porphyrin triad.

covalently linked porphyrin arrays involves multi-step synthesis and laborious column chromatographic purifications, we adopted non-covalent strategies to synthesize multiporphyrin arrays to study energy transfer at singlet state.[16] We prepared Re(I) bridged two homo dyads such as **7** containing two N_3O porphyrin subunits and **8** containing two N_3S porphyrin subunits and one hetero dyad **9** containing one N_3O porphyrin and N_3S porphyrin subunits as shown in chart 3. The dyads **7–9** were prepared in one flask by treating 0.5 equivalent of 5,10-diphenyl-15,20-di(4-pyridyl)-21-oxaporphyrin (*cis*-N_3ODPyP) and 5,10-*bis*(4-octyloxyphenyl)-15,20-*bis*(4-pyridyl)-21-thiaporphyrin (*cis*-N_3SDPyP) with 1 equivalent of $Re(CO)_5Cl$ in THF at refluxing temperature for 12 h (scheme 3). The reaction led to the formation of three dyads **7–9** which were separated by silica gel column chromatography. The dyads **7–9** showed similar ^{1}H NMR spectral features as observed for Hupp's dyads. The fluorescence properties of dyads **7–9** were investigated by both steady state and time-resolved fluorescence spectroscopic techniques and the normalized steady state fluorescence spectra of dyads **7–9** recorded at $\lambda_{ex} = 420$ nm in toluene is shown in figure 3. The steady state and time-resolved fluorescence studies on dyad **9** containing N_3O and N_3S porphyrin subunit supported the energy transfer from N_3O porphyrin subunit to N_3S porphyrin subunit. We also recently synthesized two more examples of Re(I) bridged porphyrin dyads **10** and **11** (chart 4) under similar reaction condition. The fluorescence spectra of dyad **10** containing ZnN_4 and N_3S porphyrin subunits recorded at 550 nm is shown in figure 4.

The dyad **10** on excitation at 550 nm where ZnN_4 porphyrin subunit absorbs strongly, the emission



Scheme 5. Synthesis of Re(I) bridged unsymmetrical porphyrin triad containing three different porphyrin subunits.

from ZnN_4 porphyrin was quenched by 98% and strong emission was observed from N_3S porphyrin subunit supporting an efficient energy transfer from ZnN_4 porphyrin subunit to N_3S porphyrin subunit. Hupp and co-workers[19] synthesized new type Re(I) bridged rectangle shaped porphyrin dyads **12** and **13** (scheme 4). Stoichiometric reaction of 5,15-*bis*(4-ethynylpyridyl)porphyrinato zinc(II) with either $[Re_2(CO)_6Cl_2(\text{m-bipyrimidine})]$ or $[Re_2(CO)_8\{\text{m-}bis\ (\text{benzimidazolate})\}]$ in THF at refluxing temperature gave rectangle shaped Re(I) bridged porphyrin dyads **12** and **13** respectively in decent yields. The X-ray structure solved for porphyrin dyad **13** showed an unusual collapsed structure that places the two porphyrin faces in very close proximity and substantially distorts two of the four nominally rigid ethynylpyridyl linkages. The bent geometry of the nominally rigid ethynylpyridyl-porphyrin ligand edges, mandated by the collapse of the rectangle imparts significant charge-transfer character to the rectangles Soret and Q-band region electronic

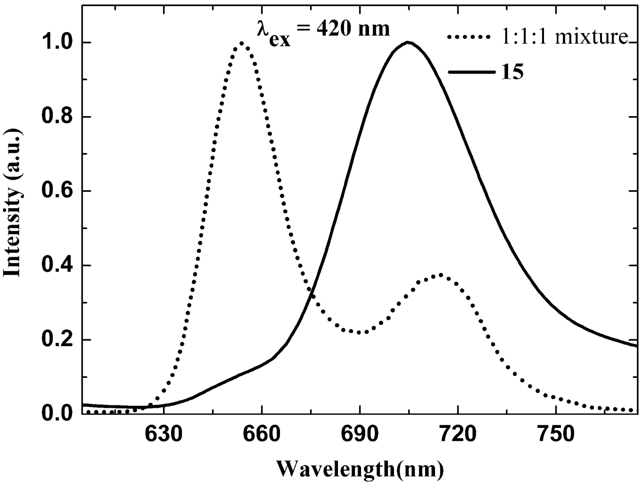
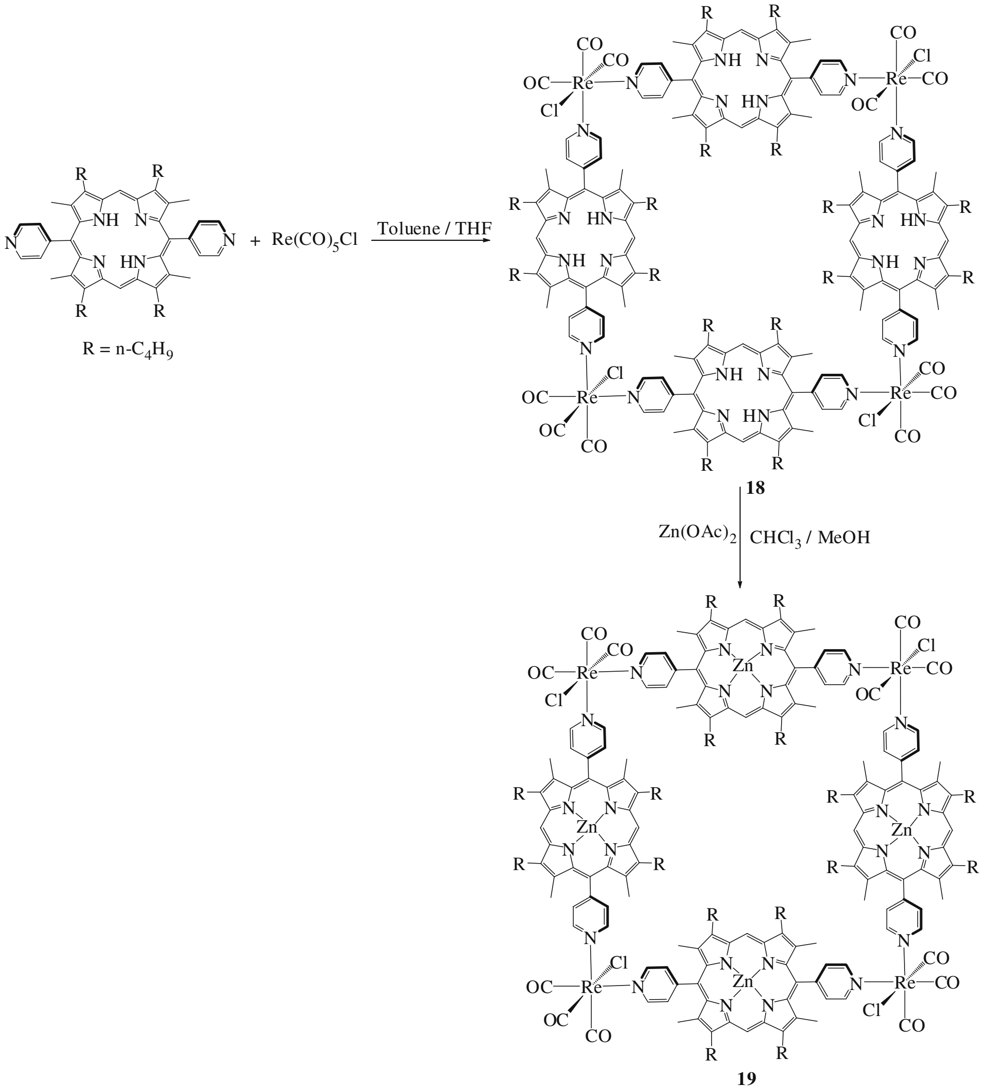


Figure 5. Comparison of fluorescence spectra of triad **15** and its 1:1:1 mixture of porphyrin monomers recorded at λ_{ex} = 420 nm in toluene.

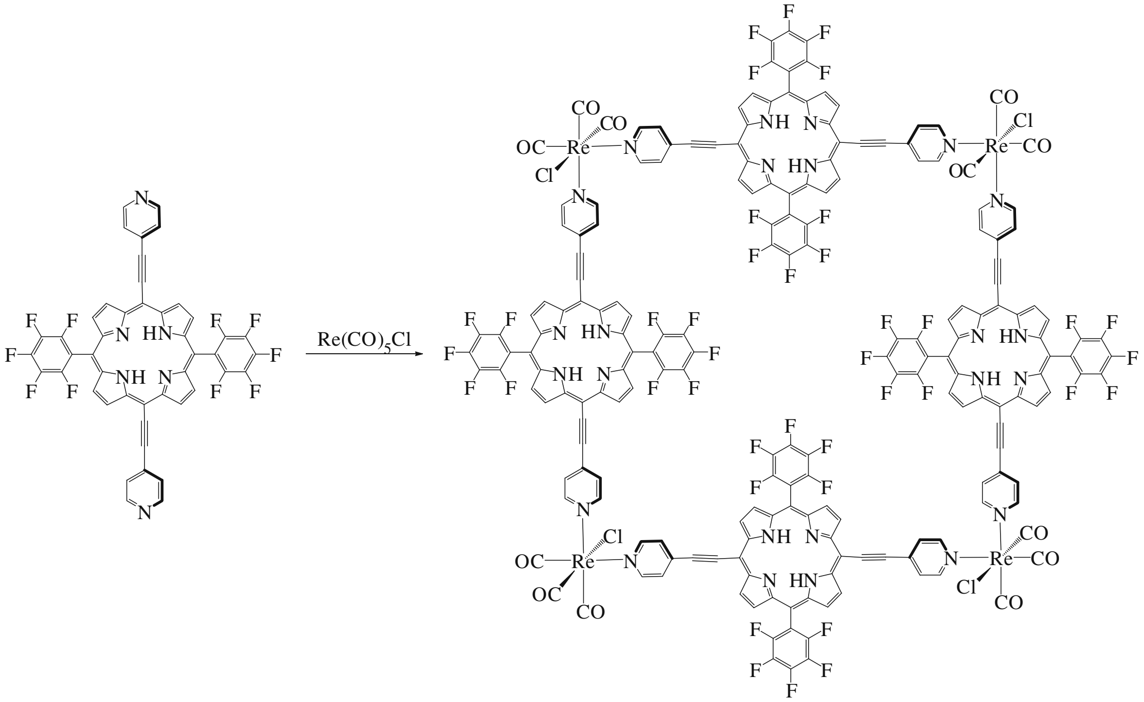


Scheme 6. Synthesis of Re(I) bridged porphyrin squares **18** and **19**.

transitions which was demonstrated experimentally by Stark spectroscopy and transient DC photoconductivity measurements and also by electronic structure calculations.

2.2 *Re(I) bridged porphyrin triads*

There are no reports yet available on Re(I) bridged porphyrin traids. However, Hupp has proposed[12] that the porphyrin triad such as **14** shown in chart 5 can be synthesized by reacting two equivalents of *cis*-*meso*-dipyridylporphyrins with one equivalent of *meso*-tetrapyridylporphyrin in the presence of Re(CO)$_5$Cl under similar reaction conditions used for the preparation of Re(I) bridged porphyrin dyads described above. We recently[20] attempted to synthesize a porphyrin triad containing three different porphyrin subunits connected using covalent and non-covalent interactions. The synthesis of N$_2$S$_2$- N$_3$S-Re(I)-N$_4$ porphyrin triad **15** is shown in scheme 5. The covalently linked porphyrin dyad **16** is reacted with *cis*- DPyN$_4$P in the presence of Re(CO)$_5$Cl in THF at refluxing temperature for overnight. The reaction resulted in the formation of mixture of three Re(I) bridged porphyrin arrays such as Re(I) bridged N$_4$-N$_4$ porphyrin dyad **1**, the required Re(I) bridged N$_2$S$_2$-N$_3$S-Re(I)-N$_4$ porphyrin triad **15** and Re(I) bridged N$_3$S-N$_2$S$_2$-Re(I)-N$_2$S$_2$-N$_3$S porphyrin tetrad **17**. The mixture was separated by silica gel column chromatography and confirmed by mass and various spectroscopic techniques. The steady state fluorescence properties of triad **15** and its 1:1:1 mixture of porphyrin monomers was investigated in detail



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Scheme 7. Synthesis of Re(I) bridged porphyrin square **20**.

and the comparison of fluorescence spectra of triad **15** along with its corresponding 1:1:1 mixture of porphyrin monomers recorded at 420 nm is shown in figure 5. On excitation of triad **15** at 420 nm where N_4 porphyrin subunit absorbs strongly, the emission from N_4 porphyrin subunit was quenched significantly and strong emission was noted from N_2S_2 porphyrin subunit. However in 1:1:1 mixture of porphyrin monomers, on excitation at 420 nm, the emission was noted mainly from N_4 porphyrin. Thus, these results suggest that in triad **15**, there is an efficient transfer occurs from N_4 porphyrin subunit to N_2S_2 porphyrin subunit mediated by N_3S porphyrin subunit. We are exploring the time-resolved photodynamics of this novel triad and efforts are on the way to construct more such Re(I) bridged porphyrin triads containing three different porphyrin subunits.

2.3 *Re(I) bridged porphyrin tetrads*

The first porphyrin square featuring *fac*-Re(CO)$_3$Cl corners has been described by Slone and Hupp in 1997.[21] Reaction of one equivalent of 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-*bis*(4-pyridyl)porphyrin with one equivalent of Re(CO)$_5$Cl in 4:1 THF/toluene at refluxing temperature for 48 h under nitrogen atmosphere followed by precipitation with hexane yielded Re(I) porphyrin square **18** in 86% yield (scheme 6). The tetrazinc(II)-metallated square **19** was prepared by reacting **18** with Zn(CH$_3$COO)$_2$ under standard metal insertion conditions (scheme 6). Both squares **18** and **19** are freely soluble and stable in organic solvents such as THF, CHCl$_3$, CH$_2$Cl$_2$, etc. The squares **18** and **19** resist crystallization and they are not volatilized easily by the standard techniques employed in mass spectrometry. Infrared spectroscopy in the carbonyl stretching region was useful to identify *fac*-tricarbonyl Re(I) units and ^{1}H NMR was used to establish Re(I)-pyridine coordination. However, these techniques were insufficient to establish square geometry of **18** and **19**. In at least one case, vapor phase osmometry has been used to confirm tetramer formation.[22] Gel permeation chromatography has been used for determining sizes of squares and for distinguishing squares from triangles since retention times vary inversely with size.[23] Pulsed-field-gradient NMR, which measures coefficients for self-diffusion has also been considered since the coefficients vary inversely with assembly size.[24] Hupp and co-workers[15] also synthesized Re(I) bridged porphyrin square **20** containing strongly electron withdrawing pentafluorophenyl groups at *meso*-positions (scheme 7) by reacting 5,10-*bis*(pentafluorophenyl)-15,20-di(4-pyridyl) porphyrin with Re(CO)$_5$Cl in THF for 48 h at refluxing temperature. The tetrazinc(II) derivative **21**

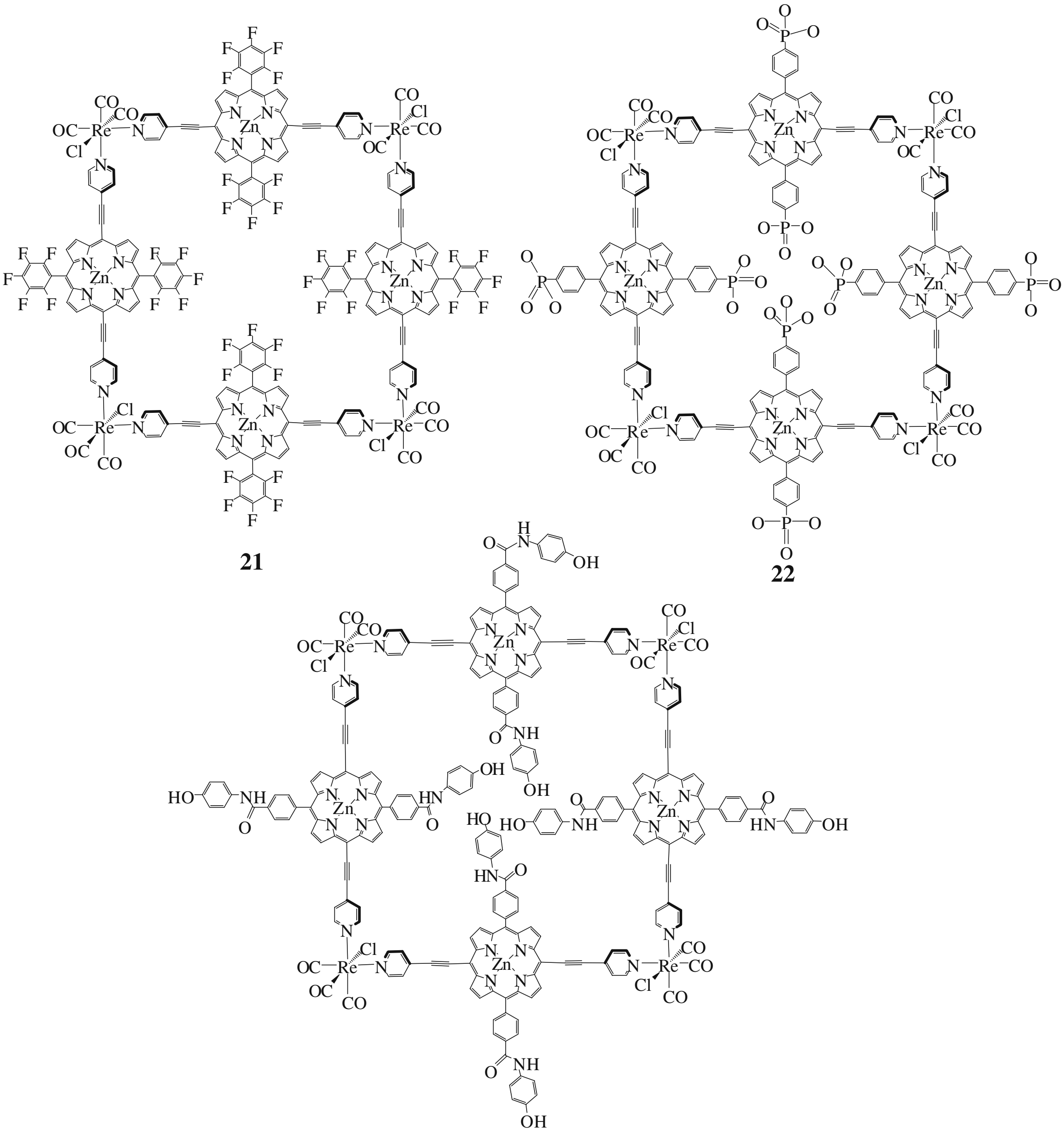

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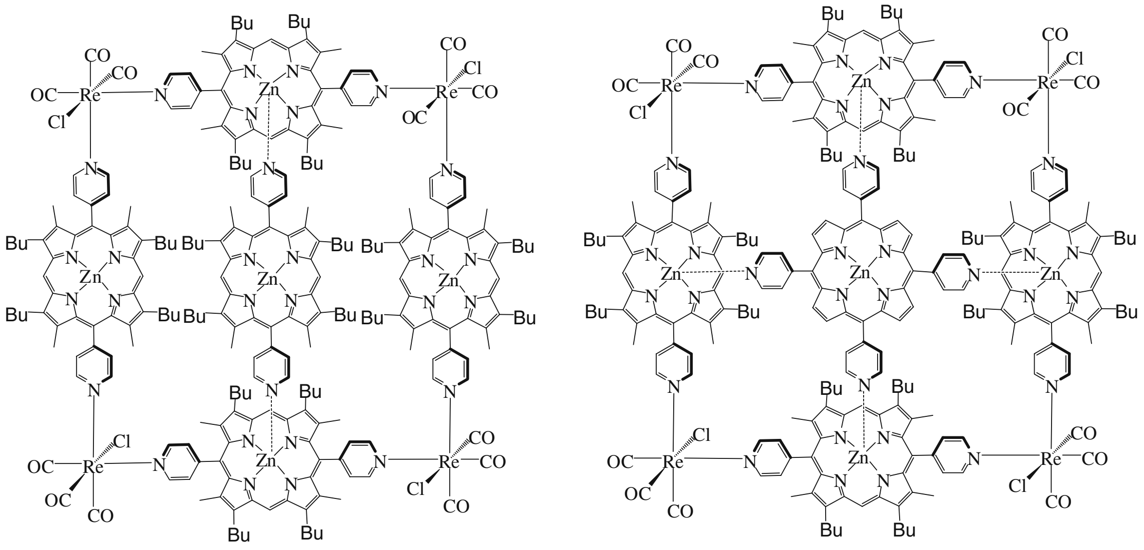
Chart 6. Re(I) bridged porphyrin squares **21–23**.

was also prepared by reacting **20** with Zn($CH_3COO)_2$ in $CHCl_3/CH_3OH$. To test the Re(I) based porphyrin squares for variety of applications, they have also synthesized phosphonate functionalized Re(I) bridged square[22] **22** as well as Re(I) bridged square containing reactive phenolic substituents[22] **23** (chart 6).

The Re(I) bridged porphyrin tetrads such as **18–23** are weakly fluorescent.[21] The singlet state lifetime is reported to be 2.4 ns. The weak luminescence and relatively short lifetime are presumably consequences of accelerated intersystem crossing caused by proximal heavy Re(I) ions. The Re(I) porphyrin tetrads **18–23** have defined cavities hence these are potential hosts for appropriate molecular guests. Belanger *et al.*[26] explored the idea of tailoring porphyrin walls by axially ligating imines, amines, and azines to the available Zn(II) centers in the porphyrin ring. The tailoring idea works, despite the affinity of Re(I) for imines and azines, because the rhenium sites are substitution inert at room temperature. Slone *et al.*[21] observed that either dipyridylporphyrin 2,8,12,18-tetrabutyl-3,7,13,17-tetramethyl-5,15-*bis*(4-pyridyl)porphyrin (DPyP) or



24 25

Chart 7. Dipyridylporphyrin and tetrapyridylporphyrin bound Re(I) bridged porphyrin squares.

tetrapyridylporphyrin 5,10,15,20-(4-pyridyl)porphyrin (TPyP) could be bound within the cavity of **19** in CH_2Cl_2 and gave pentads **24** and **25** respectively (chart 7). The association constant for two-point binding of dipyridylporphyrin was found to be about three orders of magnitude larger than one-point binding by pyridine itself. Increasing the number of Zn–N interactions to four as in the case of TPyP was found to increase the association constant by only one additional order of magnitude. Evidently, the energetic cost of arranging **19** in a box-like conformation to accommodate ligation of all four zinc ions largely offsets the gains obtained by increasing the number of ligand–metal interactions. When bound as a guest, TPyP quenched ∼90% of the luminescence of **25** and the mechanism of quenching was not established. Splan and *et al.*[15] was able to increase the binding constant for 4-(phenyl)pyridine from 1.5×10^4 to 1.35×10^5 M^{-1} in CH_2Cl_2 by using square **20** in place of square **18**. The pentafluophenyl substituents in **20** are strongly electron withdrawing, so significantly increase the lewis acidity of the Zn(II) sites and strengthen the Zn–N interaction. Recently the Re(I) bridged porphyrin squares have been explored for several applications including the fundamental aspects of light-induced energy and electron transfer.[27] Films and membranes displaying molecular-scale porosity was generated from squares **22** and **23** by van der Waals aggregation, layer-by-layer assembly chemistry based on zirconium–phosphonate links or polymerization at liquid–liquid interfaces.[25] In addition to molecular sieving, the films, membranes[28] and free assemblies of Re(I) bridged porphyrin squares **18–23** have been used for chemical sensing,[27] oxidative catalysis[29] and light-to-electrical conversion.[12]

3. Conclusions

In this paper, a brief review of Re(I) bridged porphyrin dyads, triads and tetrads is presented. Although various metals such as Ru(II), Pd(II), Pt(II), etc. have been used extensively to construct metal mediated porphyrin assemblies, the Re(I) mediated porphyrin assemblies occupied special place because of their interesting photophysical properties. In metal mediated porphyrin assemblies, most of the metals quenches the fluorescence of porphyrins but Re(I) despite being heavy metal ion, does not quench the fluorescence of porphyrin significantly and allow us to study electron and energy transfer reactions. The Re(I) bridged porphyrin dyads and tetrads containing one type of porphyrin subunit are constructed easily under simple reaction conditions, but the dyads containing two different porphyrin units requires laborious chromatographic purification. The Re(I) bridged dyads containing two different types of porphyrin subunits have been used for singlet–singlet energy transfer studies and Re(I) bridged metal containing porphyrin squares have been explored to large extent for host–guest binding studies, catalysis, chemical sensing, molecular sieving and photocurrent production studies. We hope that in future the chemistry of Re(I) based porphyrin arrays would grow rapidly and the potential of these systems for real world applications would be studied.

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