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Review

Hetero-arrays of porphyrins and phthalocyanines

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Contents

Abstract

Hetero-arrays of porphyrins and phthalocyanines have received considerable attention due to their novel composition, intriguing spectroscopic, photophysical, and redox properties, and potential application in light-harvesting and optoelectronic devices. The tetrapyrrole components, which can be held by covalent and various non-covalent linkages, may exhibit strong interactions through efficient photo-induced electron and/or energy transfer processes. The purpose of this article is to provide a comprehensive and up-to-date review of this novel class of macrocyclic compounds.

Keywords: Porphyrins; Phthalocyanines; Supramolecular complexes; Electron transfer; Energy transfer

1. Introduction

Porphyrins and phthalocyanines (Plate 1) are structurally related macrocyclic compounds. Porphyrins are naturally occurring pigments, which play an important role in various biological processes such as dioxygen transport and many redox transformations with haem-proteins [1]. Phthalocyanines are traditional industrial dyes [2], but their applications have been extended to various technological avenues. To name a few, phthalocyanines are being used as molecular electronic devices [3], optical recording materials [4], catalysts for oxidative degradation of pollutants [5,6], and photosensitizers

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Abbreviations: acac, acetylacetonate; AQ, substituted anthraquinone; dba, dibenzylideneacetone; DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; DDQ, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone; DIBAL-H, diisobutylaluminium hydride; DMA, *N*,*N*-dimethylacetamide; DMAE, *N*,*N*-dimethylaminoethanol; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; LB, Langmuir–Blodgett; OAc, acetate; Pc, dianion of phthalocyanine; Por, dianion of a general porphyrin; TMPP, dianion of *meso*-tetrakis(4-methoxyphenyl)-porphyrin; TPP, dianion of *meso*-tetraphenylporphyrin; XANES, X-ray absorption near edge structure

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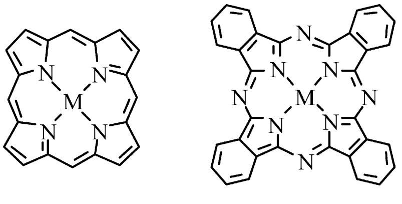


1 **2**

Plate 1. General structures of porphyrins (**1**) and phthalocyanines (**2**).

for photodynamic therapy [7,8]. The intrinsic interest of these two classes of compounds together with their widespread applications have fascinated scientists over the last few decades, leading to a substantial progress in their research.

Owing to their highly conjugated π systems, both porphyrins and phthalocyanines show intense absorptions in the visible region. The former exhibit a strong Soret band at ca. 410–450 nm together with a number of weaker Q bands at ca. 500–600 nm, while the latter show the corresponding absorptions at ca. 320–360 and 670–700 nm, respectively. The photophysical as well as the redox properties of these two classes of macrocycles are also very different despite their structural similarity, and these properties can be altered readily by the choice of the metal center and the peripheral substituents.

Recently, there has been a considerable interest in hetero-arrays of these tetrapyrrole derivatives. The resulting hybrids can display the complementary absorptions of individual chromophores, covering a large part of the solar spectrum. The components may also interact through photo-induced electron and/or energy transfer pathways. These properties are important in applications such as light harvesting, photovoltaics, and molecular photonics. A substantial number of mixed porphyrin–phthalocyanine arrays have been reported. Most of the hybrids are linked either in a covalent manner or through a large metal center forming double-decker or triple-decker complexes. Other types of linkage include bridging ligation, electrostatic interactions, axial coordination, and other supramolecular interactions. This review aims to provide an overview of the current status in the research of these mixed tetrapyrrole systems. Since heteroleptic porphyrinato and phthalocyaninato sandwich-type complexes have been comprehensively reviewed recently [9–11], this class of hetero-arrays will not be included. The chemistry of several μ-nitrido and μ-oxo bi- and tri-metallic complexes of formula [(TPP)M–N–M′(Pc)] (M = Fe, Mn; M′ = Fe, Ru; TPP = dianion of *meso*-tetraphenylporphyrin; Pc = dianion of phthalocyanine), [(TMPP)(O)Ru–O–Fe(Pc)L] [TMPP = dianion of *meso*-tetrakis(4-methoxyphenyl)porphyrin; L = monodentate ligand], and [L(Pc)Fe–O–Ru(TMPP)–O–Fe(Pc)L] has also been summarized [12,13], and is therefore also not covered in this article. Tran-Thi published a review article of similar topic in 1997, focusing on the self-assembled ionic systems [14]. Hence only the recent works not mentioned in that article are included in this review.

2. Covalently linked hetero-arrays

2.1. Dyads

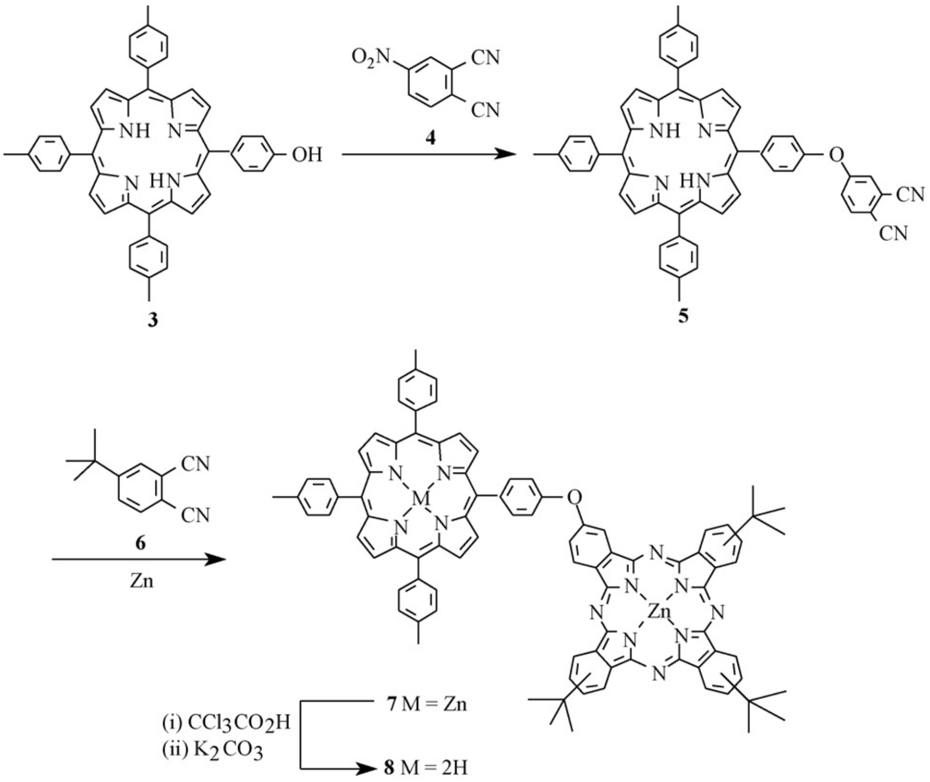
The first covalently linked hetero-arrays of porphyrins and phthalocyanines were reported by Maillard and co-workers in 1986 [15]. They treated hydroxyporphyrin **3** with 4-nitrophthalonitrile (**4**) to obtain the porphyrin-substituted phthalonitrile **5**. This compound was then condensed with an excess of 4-*tert*-butylphthalonitrile (**6**) in the presence of zinc powder as a reducing agent to afford the dyad **7**, which was purified by preparative HPLC. Upon treatment with dilute trichloroacetic acid, this compound underwent selective demetallation at the porphyrin site giving the mixed dyad **8** (Scheme 1).

The electronic absorption spectra of these dyads in toluene are very similar to those of an equimolar mixture of zinc(II) or metal-free *meso*-tetra(*p*-tolyl)porphyrin and zinc(II) tetra(*tert*-butyl)phthalocyanine. This suggests that the ground-state interaction between the two chromophores is not significant.

Upon selective excitation of the porphyrin chromophore at 424 nm in toluene, the dyad **7** shows a greatly reduced fluorescence due to the porphyrin unit (at 600 and 644 nm) concomitant with a strong emission due to the phthalocyanine moiety (at 690 nm) [16]. This indicates the occurrence of a very efficient intramolecular energy transfer process, from the excited porphyrin to the phthalocyanine core. The excitation spectrum and the ground-state absorption spectrum are virtually identical, showing that the energy transfer is nearly quantitative. From the fluorescence quantum yield and lifetime values, the quantum yield of the singlet–singlet energy transfer process ($\Phi_{\mathrm{ET}}^{\mathrm{SS}}$) was determined to be 0.87 ± 0.03. In addition to the singlet–singlet energy transfer, the triplet–triplet energy transfer process was also revealed using nanosecond absorption spectroscopy. The corresponding quantum yield ($\Phi_{\mathrm{ET}}^{\mathrm{TT}}$) was found to be 0.88 ± 0.26. These comparable and high values suggest that both singlet–singlet and triplet–triplet energy transfer processes are the main routes of depopulation of the porphyrin excited state in the dyad. Once the energy is transferred, the energy dissipative pathways of the singlet and triplet states of the phthalocyanine moiety of **7** remain the same as those of zinc(II) tetra(*tert*-butyl)phthalocyanine as indicated by their same singlet and triplet lifetimes.

In dimethyl sulfoxide (DMSO), the energy transfer pathways of **7** become less efficient ($\Phi_{\mathrm{ET}}^{\mathrm{SS}} = 0.12 \pm 0.06$, $\Phi_{\mathrm{ET}}^{\mathrm{TT}} = 0.59 \pm 0.12$), while an electron transfer process occurs predominantly with a quantum yield (Φ_{eT}) of 0.84 ± 0.30. The different behavior was explained in terms of conformational change of the dyad due to the nature of solvent interactions [16].

A series of porphyrin and phthalocyanine dyads linked by a flexible alkyl chain (compounds **9**, $n = 2$–5, Plate 2) were also prepared by standard *O*-alkylation [17]. As shown by absorption spectroscopy, there is a weak exciton interaction between the two chromophores of these dyads in the ground state in benzene. The interaction becomes stronger as *N*,*N*-dimethylformamide (DMF) is added. The dyads also exhibit intramolecular energy transfer from the excited porphyrin unit to the phthalocyanine ring. The efficiency is slightly higher for **9** ($n = 5$) on the basis of



Scheme 1. Preparation of mixed porphyrin–phthalocyanine dyads **7** and **8**.

its stronger phthalocyanine emission ($\Phi_{\mathrm{ET}}^{\mathrm{SS}} = 0.38$ in benzene). Energy transfer in this complex, however, is less favorable than that in the oxo-bridged analogue **10** ($\Phi_{\mathrm{ET}}^{\mathrm{SS}} = 0.73$ in benzene) as a result of the greater conformational flexibility and larger separation between the two chromophores [18].

In addition to the energy transfer process, an intramolecular electron transfer also takes place for these dyads, when either the phthalocyanine or the porphyrin subunit is excited. For **9** ($n = 5$), the singlet–singlet energy transfer quantum yield ($\Phi_{\mathrm{ET}}^{\mathrm{SS}}$) decreases from 0.38 to 0.08 as the solvent changes from benzene to benzene/DMF (v/v, 1:1), while the electron transfer efficiency (Φ_{eT}) increases from 0.51 to 0.86 [19]. It is likely that as the solvent polarity increases, the charge-separated state is stabilized, which promotes the electron transfer process. Concomitantly, the competitive energy transfer pathway is somewhat inhibited.

The nonlinear optical properties of **9** ($n = 2$–5) were also studied [20]. Their third-order susceptibilities χ^3 were measured by degenerate four-wave mixing method in toluene. The values [$(2.1$–$5.3) \times 10^{-11}$ esu] are slightly higher than those of the metal-free porphyrin (1.9×10^{-11} esu) and phthalocyanine (0.9×10^{-11} esu) components, and the highest value is attained for **9** ($n = 3$).

Xu and co-workers also reported another porphyrin–phthalocyanine dyad **11**, which contains a relatively more rigid piperazine spacer [21]. The synthetic route to this compound is shown in Scheme 2. Reaction of phthalonitrile **12**, prepared by treating 4-nitrophthalonitrile (**4**) with piperazine, with porphyrin **13**, generated in situ from the corresponding carboxylic acid, in the presence of 4-*N*,*N*-dimethylaminopyridine as catalyst affords the condensation product **14**. The com-

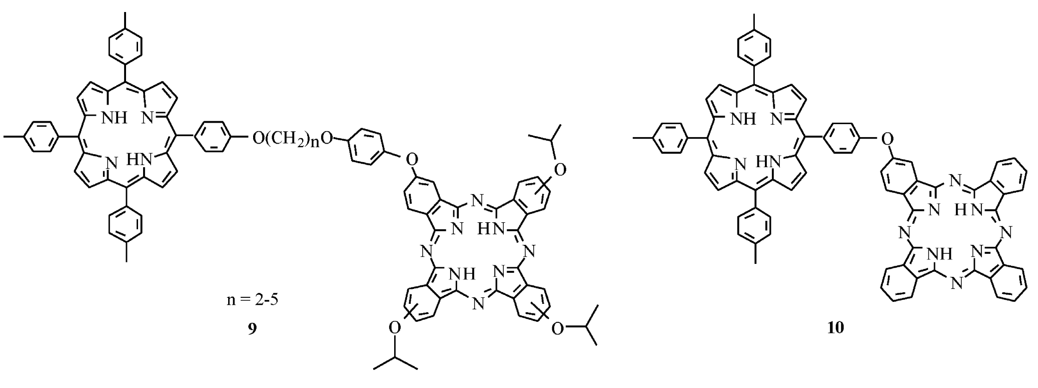
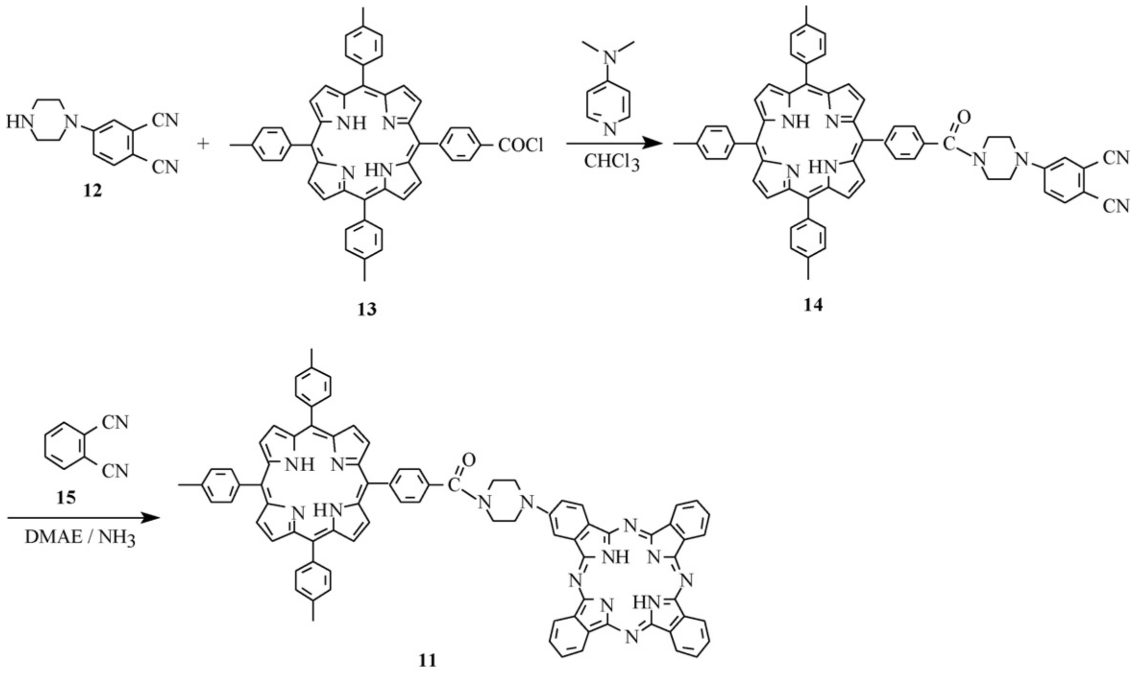


Plate 2. Structures of hetero-dyads **9** and **10**.



Scheme 2. Preparation of piperazine-bridged porphyrin–phthalocyanine dyad **11**.

pound then undergoes mixed cyclization with an excess of unsubstituted phthalonitrile (**15**) in the presence of ammonia in *N*,*N*-dimethylaminoethanol (DMAE) to give the dyad **11**. This compound exhibits similar photophysical behavior to that of **9**, but its electron transfer efficiency in DMF is significantly higher than that of the hetero-dyads linked by oxygen or the flexible alkoxy chains. This facile process is in accord with the negative free energy change (ΔG^0_{eT}) estimated by the Rehm–Weller equation, assuming that the piperazine adopts a boat instead of a chair conformation. This conformation can bring the two chromophores in close proximity facilitating the electron transfer process.

As a photosynthetic model compound, the anthraquinone-substituted porphyrin–phthalocyanine dyad **16** (Plate 3) was prepared by mixed cyclization of porphyrin-substituted phthalonitrile **5** with 4-(4-hydroxyphenoxy)phthalonitrile in the presence of anhydrous $Zn(OAc)_2$ followed by the reaction with 2-bromomethyl anthraquinone [22]. As shown by absorption spectroscopy, the three chromophores do not act entirely as independent units and weak interactions among them were revealed. Upon laser excitation at 355 nm, the dyad **16** in DMF shows a photo-induced intramolecular electron transfer from the porphyrin unit via the phthalocyanine core to anthraquinone, giving rise to the radical pair $\mathrm{Zn(Por)}^{\bullet +}\text{–}\mathrm{Zn(Pc)}\text{–}\mathrm{AQ}^{\bullet -}$ (Por = dianion of a general porphyrin; AQ = substituted anthraquinone).

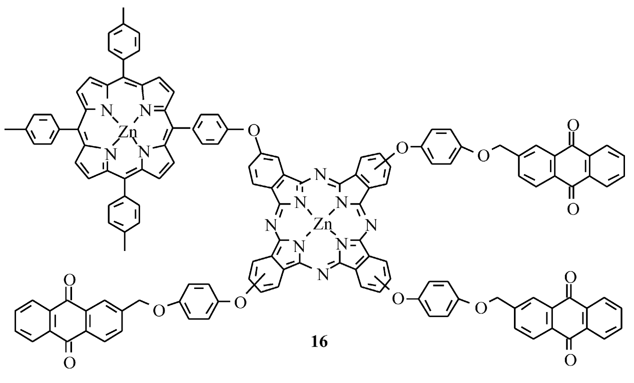
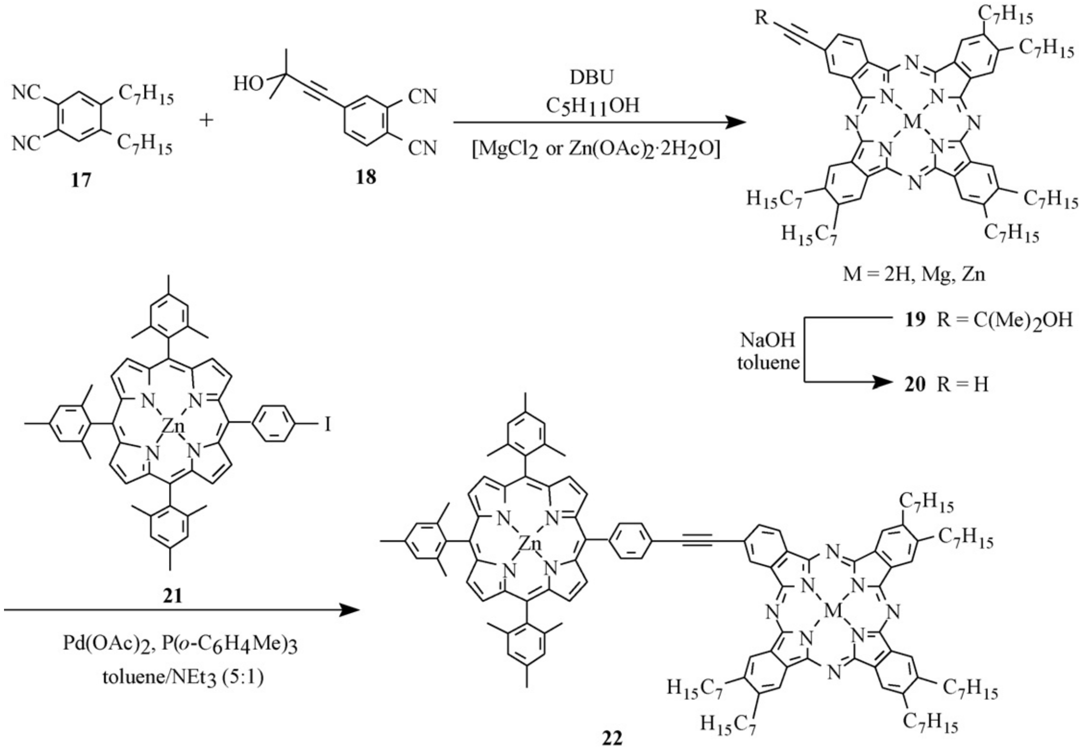


Plate 3. Structure of anthraquinone-substituted porphyrin–phthalocyanine dyad **16**.

Lindsey and co-workers also prepared a series of seven porphyrin–phthalocyanine dyads with a phenylethynyl linker [23]. Scheme 3 shows the synthetic route used to prepare these compounds. Treatment of 4,5-di-*n*-heptylphthalonitrile (**17**) with 4-(3-hydroxy-3-methylbut-l-ynyl)phthalonitrile (**18**) (1:6 ratio) in the presence of a catalytic amount of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (and $MgCl_2$ or $Zn(OAc)_2{\cdot}2H_2O$ for the preparation of the metallated analogues) in 1-pentanol affords the phthalocyanines **19** (M = 2H, Mg, Zn) in 3–28% yield. Upon treatment with NaOH in toluene, deprotection of these compounds occurs giving the ethynyl phthalocyanines **20** in ca. 85% yield. The metal-free analogue **20** (M = 2H) can also be prepared in almost quantitative yield by treating the magnesium counterpart **20** (M = Mg) with trifluoroacetic acid. Compounds **20** can then be coupled with iodoporphyrin **21** using $Pd(OAc)_2$ and tri-*o*-tolylphosphine as catalysts. The tetrapyrrole centers of the resulting dyads **22** can be changed (to 2H, Mg, or Zn) by selective metallation and demetallation.

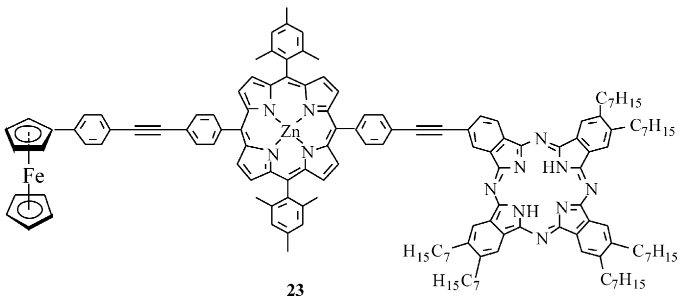
Transient absorption and steady-state emission studies of these dyads show that intramolecular singlet–singlet energy transfer from the porphyrin to the phthalocyanine moiety is very fast (≤10 ps) and efficient (≥90%), particularly for those in which competing electron transfer is inhibited on energetic grounds [23]. Electron transfer involving the excited phthalocyanine and the porphyrin units is not a favorable process (typically



Scheme 3. Preparation of phenylethynyl-linked porphyrin–phthalocyanine dyads **22**.

<10% depending on the redox properties of the chromophores). Hence for most of these dyads, strong fluorescence due to the phthalocyanine ring is observed ($\Phi_f = 0.37–0.75$), making them well suited as bright emitters in porphyrin-based molecular photonic devices.

As a model compound for fundamental studies of optoelectronic gating, compound **23** (Plate 4) was prepared from ethynyl phthalocyanine **20** (M = 2H), zinc(II) 5,15-bis(4-iodophenyl)-10,20-dimesitylporphyrin, and 4-ferrocenylphenylethyne using the aforementioned palladium-catalyzed reaction conditions [24]. The compound contains a zinc(II) porphyrin input unit, a phthalocyanine bright far-red emitting output unit, and ferrocene as a redox-switching unit. Oxidation of the latter leads to an almost complete quenching of the phthalocyanine fluorescence despite their far separation. This observation indicates that the ferrocene radical cation is a very efficient trap for the excited-state energy, and the quenching should occur via superexchange involving the intervening porphyrin unit.



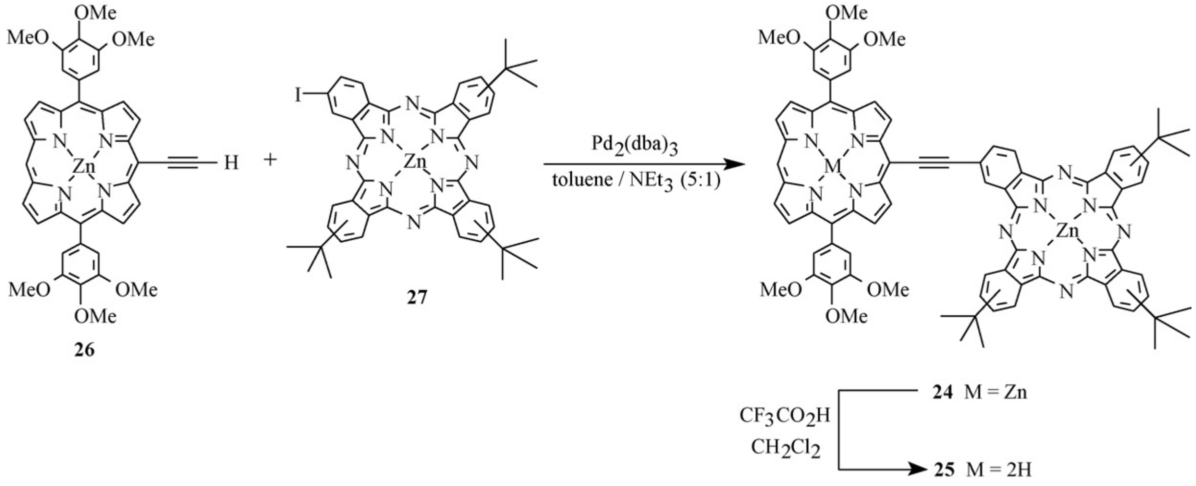
23

Plate 4. Structure of ferrocene-containing porphyrin–phthalocyanine dyad **23**.

Sutton and Boyle also prepared two related porphyrin–phthalocyanine dyads **24** and **25**, in which the two macrocycles are directly linked by a triple bond [25]. The synthesis involves a palladium-catalyzed coupling reaction of *meso*-ethynyl porphyrin **26** and iodophthalocyanine **27** (Scheme 4). The absorption spectrum of **24** in toluene shows a red-shifted Soret band (at 352 nm) compared with that of an equimolar mixture of **26** and **27** (at 342 nm). This is a strong indication of effective electronic communication between the two π systems. The phthalocyanine Q band of these dyads is also split as a result of the electronic and symmetry effects induced by the ethynyl porphyrin substituent.

Compounds **28** and **29** are related dyads connected directly at the *meso*- and β-positions of porphyrin and phthalocyanine, respectively [26]. Scheme 5 shows the synthetic route for these compounds. Mixed cyclization of the diiminoisoindolines **30** and **31** in the absence or presence of $Zn(OAc)_2$ in DMAE gives the cyano phthalocyanines **32**, which undergo reduction to give the formyl counterparts **33**. These compounds then condense with methoxycarbonylethyldipyrromethane (**34**) and 1-methylimidazole-2-carboxaldehyde (**35**) followed by oxidation with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) to afford the dyads **28** in 13–15% yield. Treatment of these compounds with $Zn(OAc)_2$ leads to metallation at the porphyrin site giving **29**.

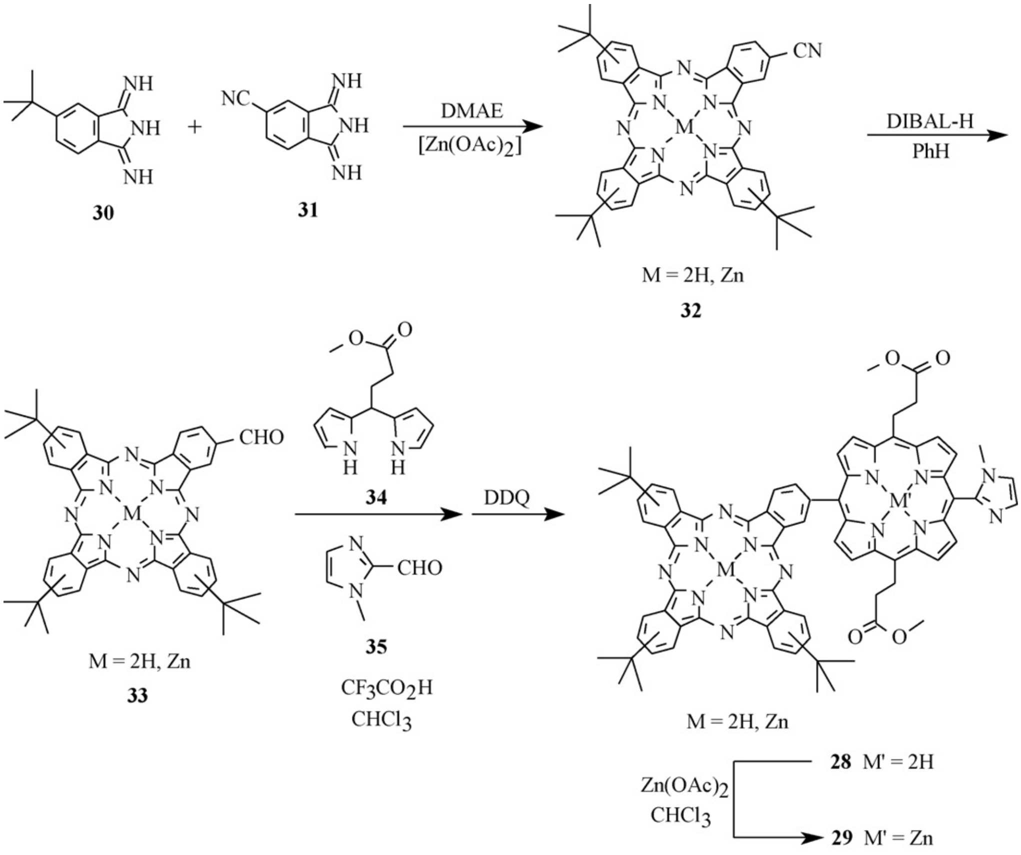
These dyads have the shortest edge-to-edge distance between the macrocycles (ca. 1.5 Å) in hetero porphyrin and phthalocyanine dyads, leading to strong excitonic coupling and very efficient energy transfer from the porphyrin to phthalocyanine moieties. Compound 28 (M = M′ = 2H), for example, gives strong fluorescence from the phthalocyanine moiety when the



Scheme 4. Preparation of ethynyl-linked porphyrin–phthalocyanine dyads **24** and **25**.

porphyrin moiety is excited (at 516 nm). The fluorescence quantum yield ($\Phi_f = 0.71$) is close to that of tetra(*tert*-butyl)phthalocyanine ($\Phi_f = 0.77$). In non-coordinating solvents such as toluene, stable complementary dimeric dyads of **29** are formed through the axial coordination of the zinc center in the porphyrin ring and the imidazolyl nitrogen atom of another molecule (Plate 5). The dimer formation is supported by the split Soret bands at ca. 410 and 440 nm, and the upfield shift of the ^{1}H NMR signals of the coordinating imidazolyl groups.

Very recently, Torres and co-workers have prepared three similar hetero-dyads **36**, in which the two chromophores are linked at the β-positions [27]. The preparation of these compounds involves a classical mixed cyclization method using the porphyrin-containing phthalonitrile **37** and the corresponding phthalonitriles (Scheme 6). Again, the close proximity of the two chromophores in these dyads results in strong through-space excitonic coupling and ultrafast energy transfer (ca. 10^{12} s^{-1}) as determined by femtosecond transient absorption studies.



Scheme 5. Preparation of directly linked porphyrin–phthalocyanine dyads **28** and **29**.

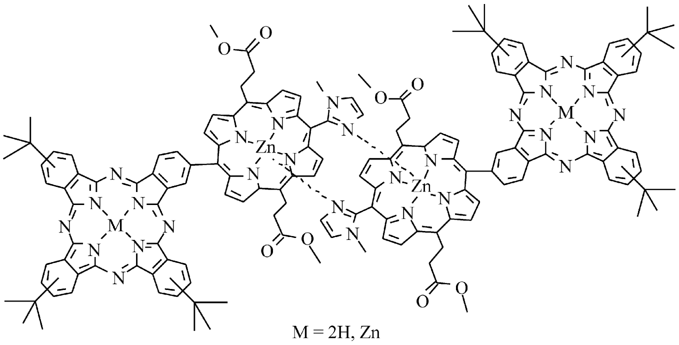


Plate 5. Proposed structure of the dimeric dyads of **29**.

2.2. *Triads*

A linear array of chromophores consisting of a perylene input unit, a bis(metal-free porphyrin) transmission unit, and a metal-free phthalocyanine output unit was synthesized by Lindsey and co-workers for studies in artificial photosynthesis and molecular photonics [28]. The preparation of this porphyrin–phthalocyanine triad **38** involves a quite lengthy procedure. First of all, two *trans*-AB_2C porphyrins (**39** and **40**) each bearing one unsubstituted *meso*-position are prepared, which undergo oxidative *meso–meso* coupling to give the bis-porphyrin **41**. After demetallation, compound **42** is formed. Having one phthalonitrile moiety and one iodophenylene group, this compound undergoes sequential mixed cyclization with 4-*tert*-butylphthalonitrile (**6**) and palladium-mediated coupling with ethynyl perylene **44** to afford **38** (Scheme 7).

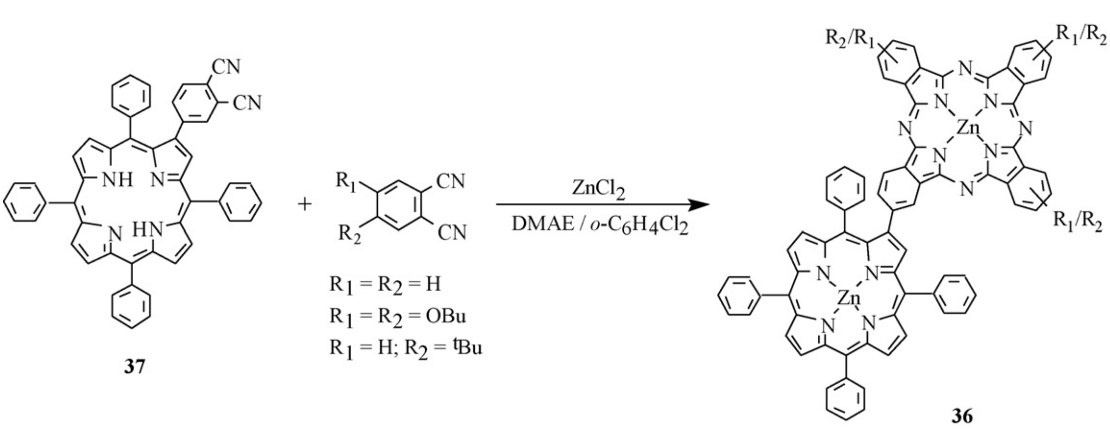
The linear array **38** absorbs strongly across much of the visible region. Upon excitation of the perylene and bis(porphyrin) components at 490 or 529 nm (with ca. 6:4 relative absorption), emission occurs almost exclusively from the phthalocyanine unit. The time constants as determined by time-resolved experiments were found to be 2 ps (90%) and 13 ps (10%), which are much shorter than the excited state lifetimes of some perylene and bis(porphyrin) model compounds (ca. 10 ns). The results indicate the presence of an extremely fast and efficient funnelling of energy from perylene through bis(porphyrin) to phthalocyanine in **38**.

Compared with other light-harvesting and energy-funnelling systems such as **45** and **46** (Plate 6), this linear array has several advantages. First of all, it has good spectral coverage across the blue and red region. It exhibits ultrafast and essentially quantitative energy transfer from the perylene end to the phthalocyanine end of the array, the emission of which is as bright ($\Phi_f = 0.78$) and long-lived ($\tau_f = 6$ ns) as in an isolated phthalocyanine model compound.

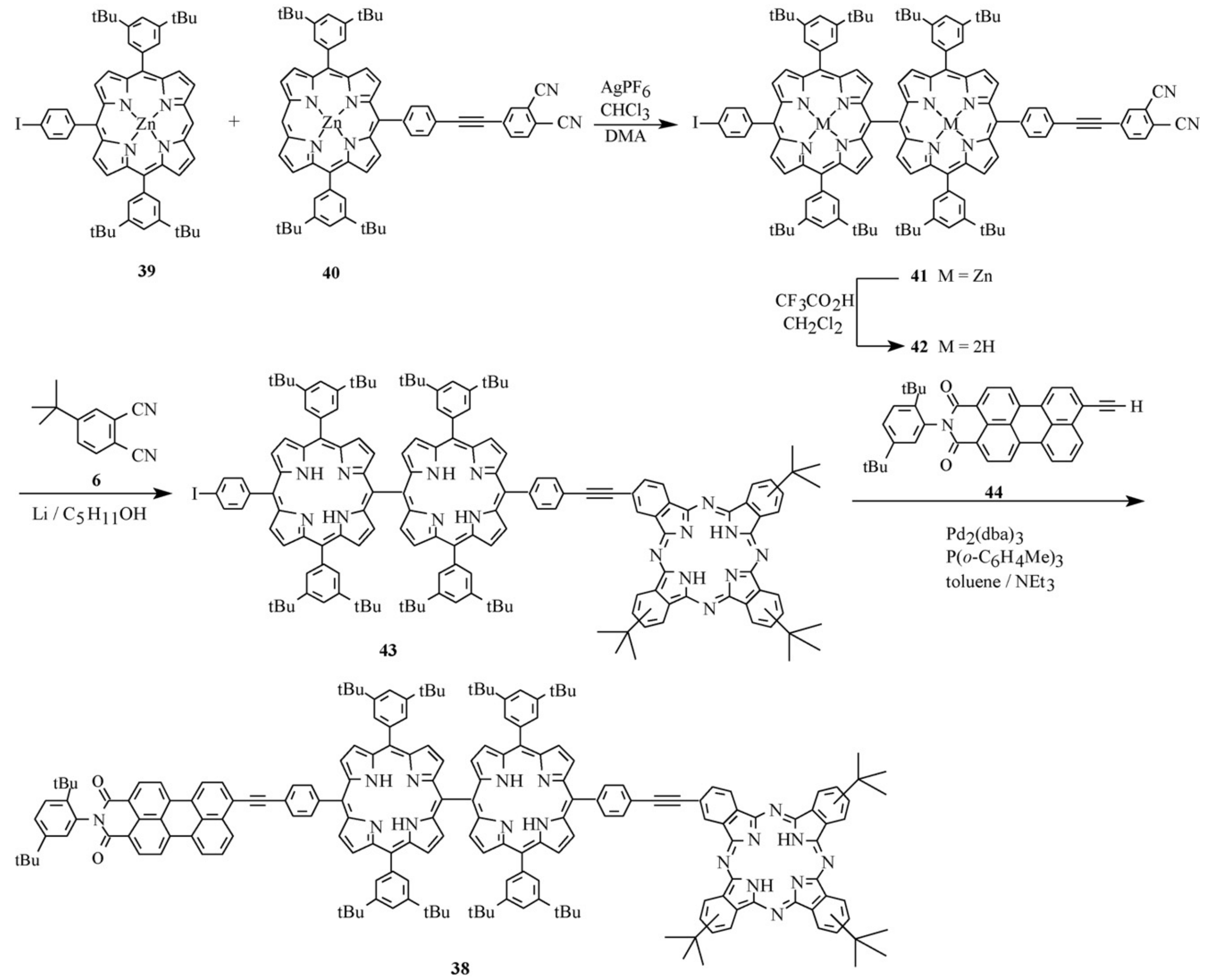
Compound **47** is another porphyrin–phthalocyanine triad linked simply by the oxo groups [29]. As shown in Scheme 8, the preparation of this compound involves three steps. First of all, reaction of hydroxyporphyrin **48** with 4,5-dichlorophthalonitrile (**49**) in the presence of K_2CO_3 leads to aromatic nucleophilic substitution giving the bis-porphyrinated phthalonitrile **50**, which can then be metallated with $Zn(OAc)_2{\cdot}2H_2O$ to give **51**. The dyad **47** can be obtained in 6% yield by ring-expansion reaction of subphthalocyanine (**52**) with **51** in the presence of DBU in DMSO.

Upon excitation at 403 nm (at a vibronic band near the Soret band of porphyrin), the triad **47** shows fluorescence emissions due to the porphyrin moieties as well as the phthalocyanine unit. The appearance of the phthalocyanine emission clearly shows an energy transfer process from the excited porphyrin units to the phthalocyanine moiety. The energy transfer quantum yield was calculated to be 0.77. As a result, the fluorescence quantum yield upon excitation at 603 nm (at the porphyrin Q band) is greatly reduced ($\Phi_f = 0.009$ versus $\Phi_f = 0.039$ for ZnTPP). The fluorescence quantum yield calculated for the phthalocyanine moiety (excitation at 640 nm) is also reduced ($\Phi_f = 0.14$ versus $\Phi_f = 0.23$ for ZnPc), which is attributed to a photo-induced electron transfer process involving the porphyrin substituents. The triplet properties of this triad were also studied by laser flash photolysis. The triplet lifetime (τ_T) and quantum yield (Φ_T) were determined to be 260 ± 30 μs and 0.10 ± 0.02, respectively, which are significantly lower than those of ZnPc ($\tau_T = 330$ μs; $\Phi_T = 0.65$) [29].

Recently, a similar approach has been employed to prepare the porphyrin-containing phthalonitriles **53** and **54** (Plate 7) [30]. These compounds undergo a mixed cyclization with unsubstituted phthalonitrile (**15**) in the presence of the half-sandwich complex [Eu^{III}(Pc)(acac)] (acac = acetylacetonate) and DBU



Scheme 6. Preparation of β-linked porphyrin–phthalocyanine dyads **36**.



Scheme 7. Preparation of perylene-substituted porphyrin–phthalocyanine triad **38**.

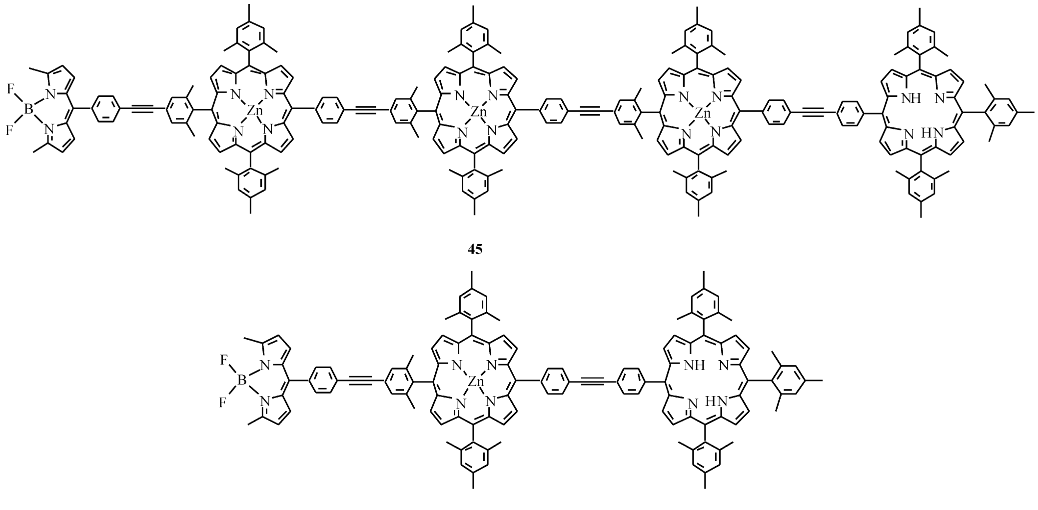
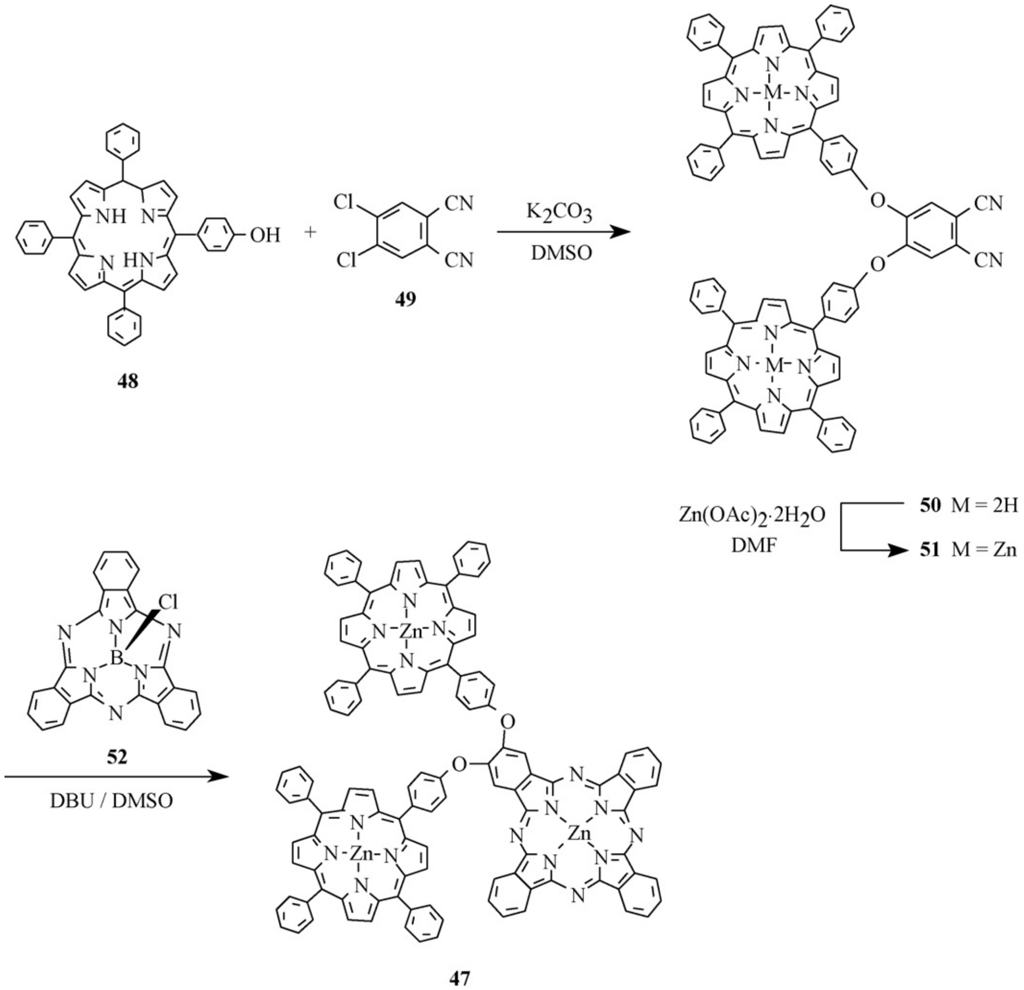


Plate 6. Structures of porphyrin arrays **45** and **46**.



Scheme 8. Preparation of hetero porphyrin–phthalocyanine triad **47**.

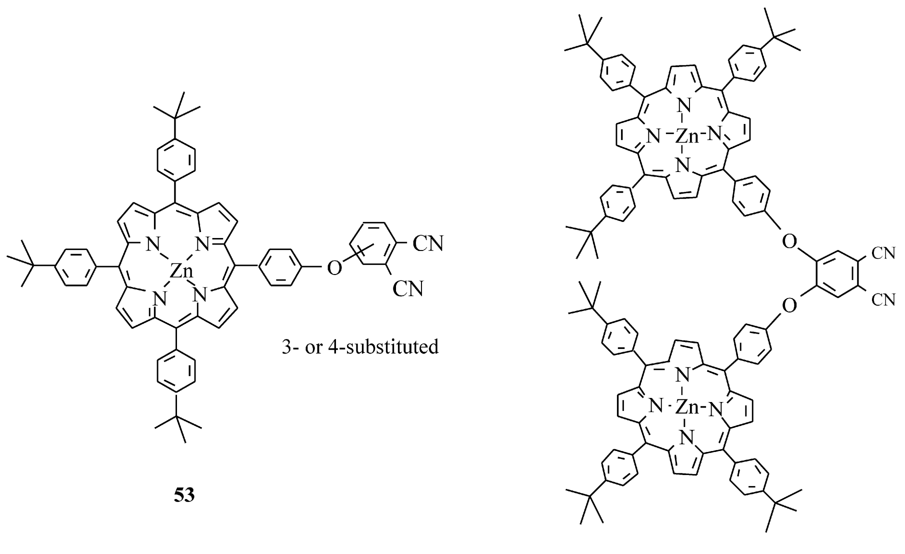


Plate 7. Structures of porphyrin-substituted phthalonitriles **53** and **54**.

to afford several novel porphyrin-appended europium(III) bis(phthalocyaninato) complexes.

Recently, we have also prepared the triad **55** (Plate 8) by treating the hydroxyporphyrin **48** with silicon(IV) phthalocyanine dichloride in toluene in the presence of pyridine [31]. Its photophysical properties in DMF have been studied in detail by steady-state absorption and fluorescence spectroscopy, femtosecond fluorescence up-conversion measurements, and picosecond transient absorption spectroscopy. The fluorescence quantum yields of both the porphyrin and phthalocyanine parts in the triad are greatly reduced compared with those of the reference compounds as a result of photo-induced electron transfer (eT) and excitation energy transfer (ET) between the two components. When the porphyrin moieties are initially excited, fluorescence due to the phthalocyanine core is observed, which is a major depopulation pathway of the first excited singlet state of the porphyrin. Electron transfer is a competitive process, but its probability is about six times lower. When the first excited singlet state of the phthalocyanine core is populated, either by direct excitation or via excitation energy transfer, it undergoes fast depopulation via electron transfer to the charge-separated state. Fig. 1 summarizes the different transitions including the rate constants of these processes.

2.3. Tetrads

To the best of our knowledge, covalently linked porphyrin–phthalocyanine tetrads remain unknown. Only a series of structurally related porphyrin–porphyrazine analogues have recently been reported [32]. The formation of these tetrads involves a stepwise “2 + 2” complexation of the exocyclic pyridyl porphyrins **56** and the geminal diamino porphyrazines **57** with two platinum(II) centers (Scheme 9). Porphyrins **56** are firstly treated with $PtCl_2(PhCN)_2$ in toluene to give the dimeric complexes **58** in high yields as a result of their favorable binding topology to form the closed supramolecular system. The removal of the chloro ligands of these complexes by $Ag(ClO_4)$ facilitates the coordination of the vacant sites by the exocyclic geminal amino groups of **57**. The tessellated arrays **59** are then obtained in ca. 60% spectroscopic yields. Palladium(II) ions can also induce similar self-assembly, but the resulting arrays are less robust than the platinum counterparts.

The electronic absorption bands of **59** in toluene are red-shifted and broadened compared with those of the individual components as a result of the edge-to-edge electronic interactions between the chromophores through the platinum(II) linkers. The fluorescence emissions of these tetrads are also red-shifted and there is substantial energy migration from the porphyrin moieties to the porphyrazines.

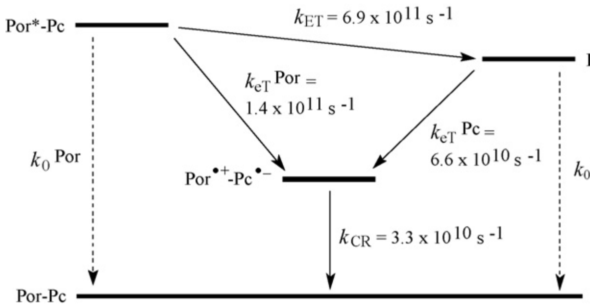
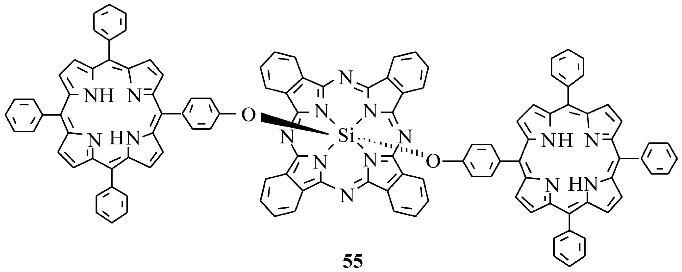


Fig. 1. Energy levels and transfer schemes of the triad **55** in DMF.



55

Plate 8. Structure of hetero porphyrin–phthalocyanine triad **55**.

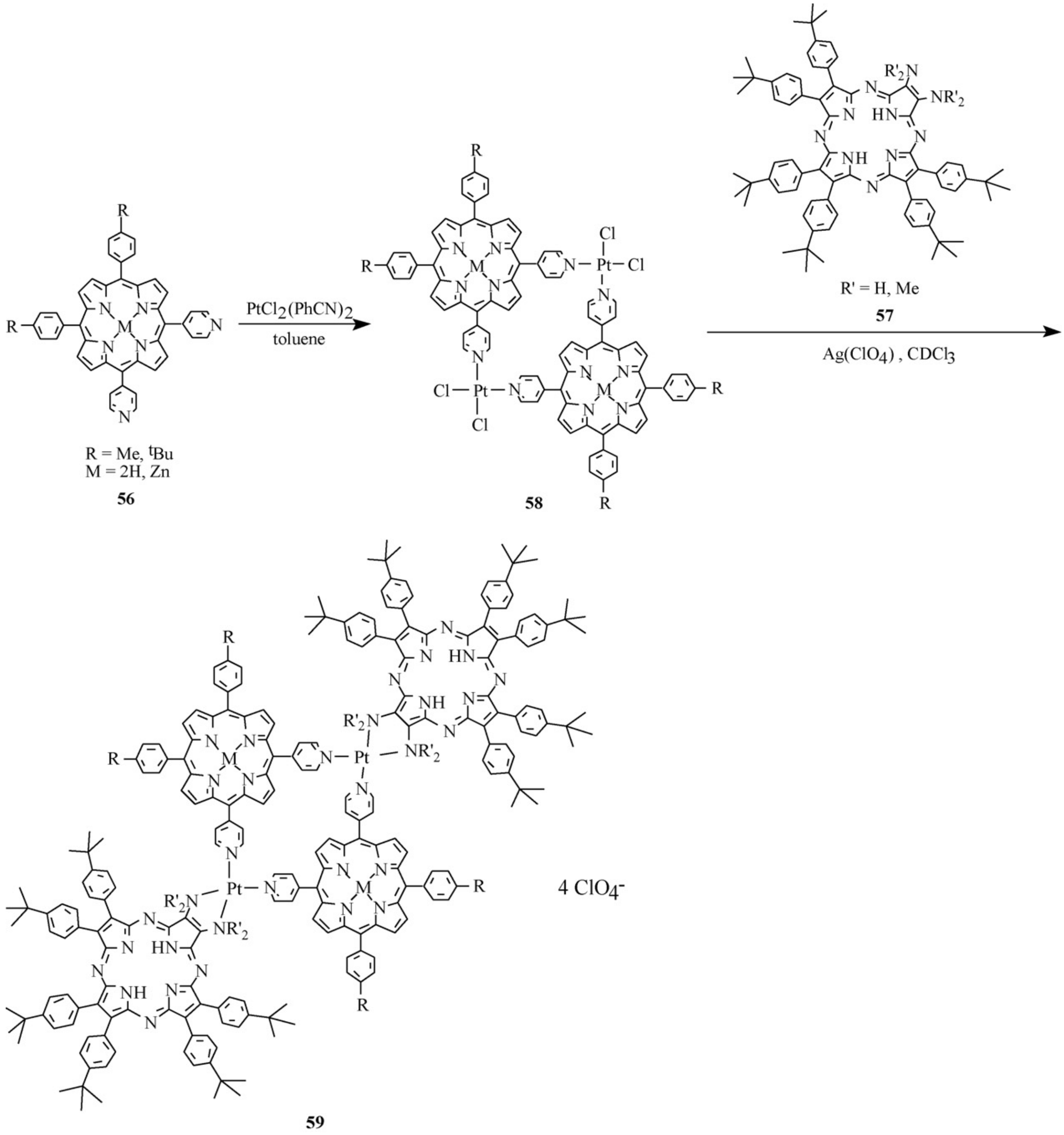
Deposition of these supramolecular complexes as drop-cast films on mica has been examined by AFM. These cationic arrays form stable and uniform ultrathin films on the anionic surface of mica, as shown by their absorption and fluorescence spectra.

2.4. Pentads

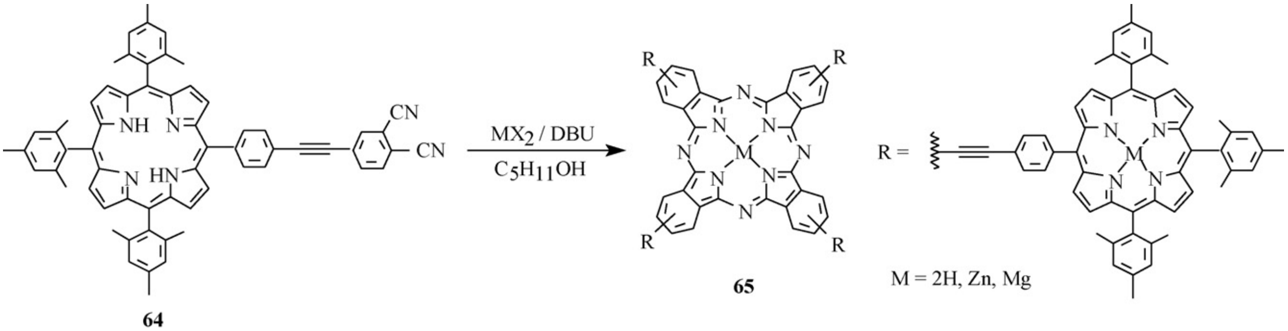
The first porphyrin–phthalocyanine pentads were reported by Kobayashi and co-workers in 1987 [33,34]. They employed the tetra-anhydride of 2,3,9,10,16,17,23,24-octacarboxyphthalocyanine (**60**) as the starting material and condensed it with 5-(4-aminophenyl)-10,15,20-triphenylporphyrin (**61**) to give the tetra-porphyrin-substituted phthalocyanine **62** (Plate 9) in 73% yield. Treatment of this compound with $FeCl_2$ in refluxing DMF affords the iron analogue **63**. The absorption spectrum of the pentad **62** in DMF shows a broader and weaker Soret band compared with the sum of the spectra of **60** and 4 equiv. of **61**, suggesting that the tetrapyrrole components have ground-state interactions.

Lindsey and co-workers prepared a related series of pentads in which four porphyrin moieties are linked to a phthalocyanine core in a star-shaped architecture through ethynyl linkers [35]. The synthesis involves a straightforward and classical based–promoted tetramerization of the porphyrin-containing phthalonitrile **64** in the presence of a metal salt (Scheme 10). Arrays with different centers (2H, Zn, or Mg) in the macrocycles can be prepared by selective metallation and demetallation. As expected, these compounds show intense absorptions in the blue and red region, and exhibit rapid (in ps) and efficient singlet–singlet energy transfer from the porphyrin moieties to the phthalocyanine core as shown by steady-state and time-resolved spectroscopic methods. For the mono-oxidized all-metal pentads, ground-state hole/electron hopping is rapid on the EPR time scale, showing that electronic communication among the components is very effective in these arrays.

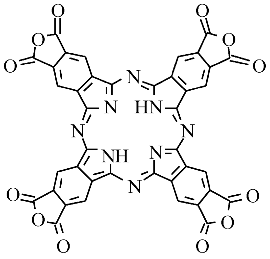
By using a similar self-cyclization method, Nyokong and co-workers also prepared the tetra-porphyrin-substituted phthalocyanines **66** [36]. As shown in Scheme 11, porphyrin **67**, which can be prepared by treating 5-(4-hydroxyphenyl)-



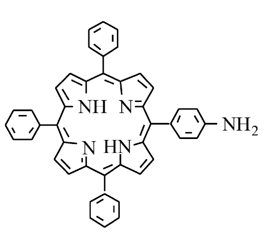
Scheme 9. Preparation of tessellated porphyrin–porphyrazine tetrads **59**.



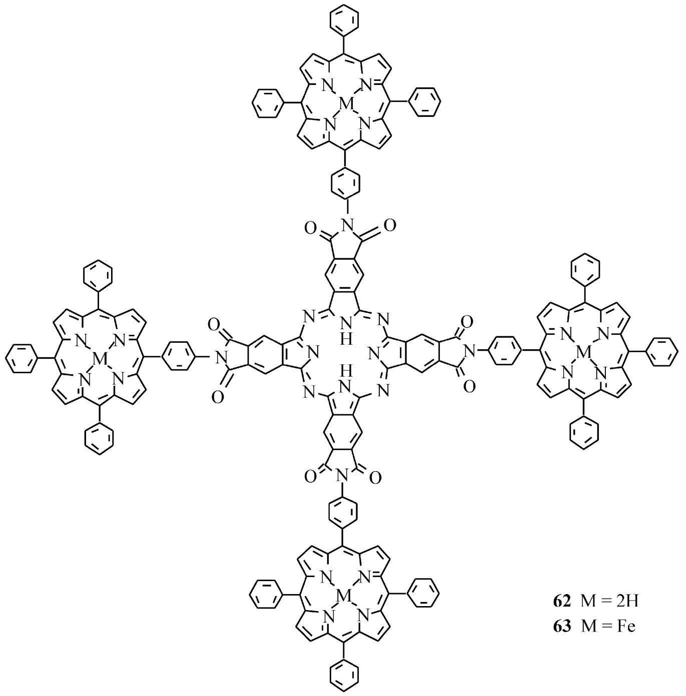
Scheme 10. Preparation of mixed porphyrin–phthalocyanine pentads **65**.



60



61



62 M = 2H
63 M = Fe

Plate 9. Structures of phthalocyanine **60**, porphyrin **61**, and mixed pentads **62** and **63**.

10,15,20-triphenylporphyrin (**48**) with 4-nitrophthalonitrile (**4**) followed by metallation with $Zn(OAc)_2{\cdot}2H_2O$, can be converted to pentad **66** (M = 2H) in 10% yield upon treatment with lithium in 1-octanol. Compound **67** can also be converted to the zinc phthalocyanine analogue **66** (M = Zn) in 16% via the diiminoisoindoline **68**.

The spectroscopic and photophysical properties of these pentads were also studied. The presence of four porphyrin substituents on the zinc(II) phthalocyanine core in **66** (M = Zn) slightly shifts the Q band from 670 nm (for ZnPc) to 678 nm in toluene. There is a mutual quenching of the singlet-excited states of both chromophores when they are selectively excited. For the phthalocyanine core, the quenching is due to electron transfer. However, for the porphyrin moieties, the quenching arises from a combination of both electron transfer and energy transfer. The efficiencies of these processes are significantly higher compared with those for a 1:4 molar mixture of ZnPc and ZnTPP. This can be attributed to the proximity of the donor and acceptor in the pentads.

By using the cobalt analogue of **68** and $Co(OAc)_2{\cdot}4H_2O$ instead of $Zn(OAc)_2{\cdot}2H_2O$ in the self-cyclization reaction, the all-cobalt analogue of **66** can be prepared [37]. This compound exhibits nine redox processes as shown by cyclic voltammetry and square wave voltammetry. Spectroelectrochemical studies reveal that the first oxidation occurs on the cobalt phthalocyanine core and the first reduction occurs on the cobalt porphyrin moieties. The subsequent reduction occurs on the phthalocyanine and porphyrin units in an alternating manner. This all-cobalt pentad can also be immobilized onto a glassy carbon electrode to form an efficient amperometric sensor for hydrogen peroxide in neutral and basic media [38]. The system shows a fast amperometric response (approximately 1 s) with linearities up to $\geq$1.50 mM. It also has a low detection limits (micromolar range) and high stability (8 weeks).

2.5. *Higher-order arrays*

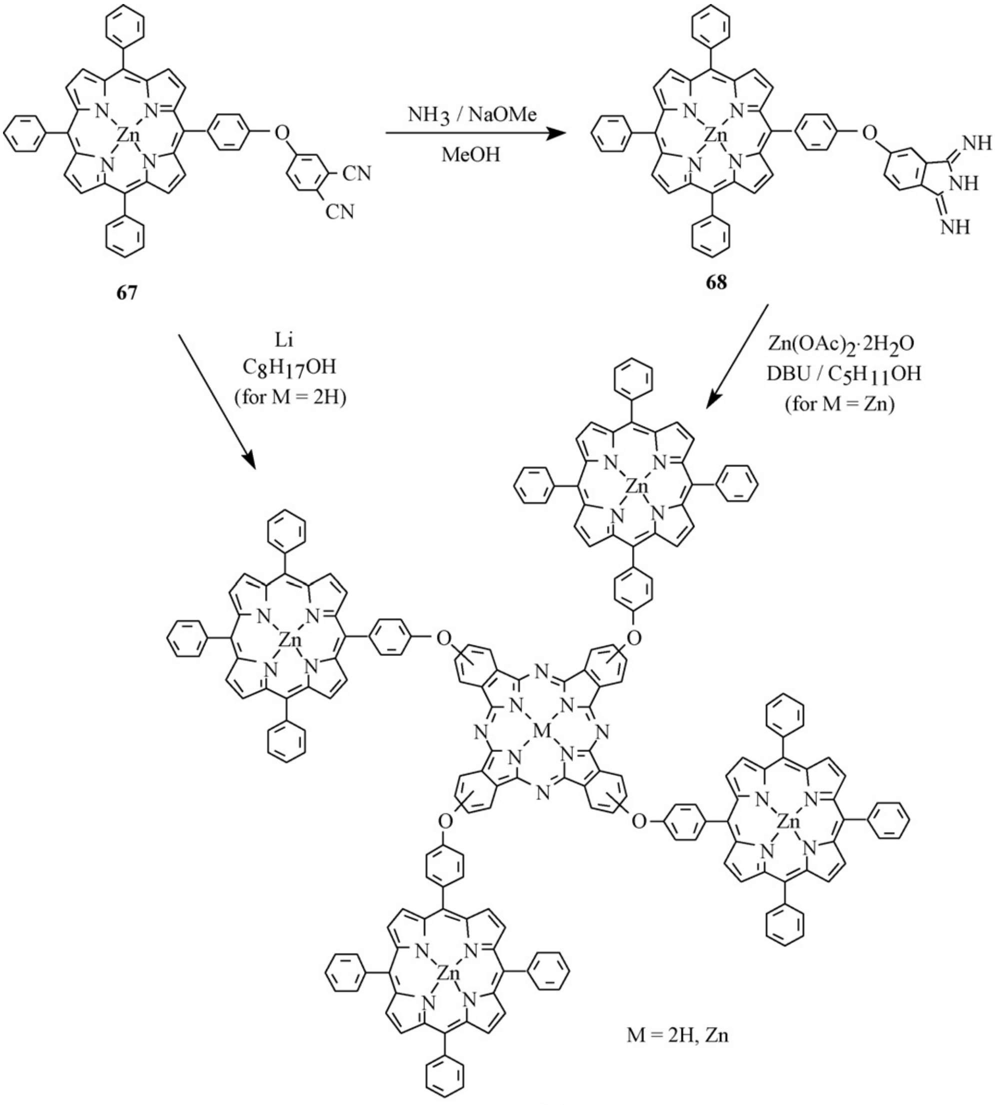
As another light-harvesting system, the star-shaped arrays **69** were also prepared by Li and Lindsey [39]. The synthesis involves a classical self-cyclization of bis-porphyrinated phthalonitrile **70**, which can be prepared by palladium-mediated coupling of the ethynylporphyrin **71** and the iodoporphyrin **72** (Scheme 12). Addition of $MgCl_2$ or $Zn(OAc)_2{\cdot}2H_2O$ during the cyclization gives the all-magnesium or all-zinc nonamer, respectively, while the use of lithium pentoxide affords the all-metal-free analogue, which can also undergo magnesium insertion to give the all-magnesium counterpart. Similar to the aforementioned porphyrin–phthalocyanine arrays prepared by the same group, these nonamers absorb strongly across the solar spectrum and exhibit efficient intramolecular singlet-excited state energy transfer from the porphyrin moieties to the phthalocyanine core.

Another hetero-nonamer of porphyrin and phthalocyanine has been reported recently [29]. This array contains a zinc(II) phthalocyanine core substituted with eight zinc(II) porphyrin units at the 2,3,9,10,16,17,23,24-positions. The synthesis involves the conversion of 4,5-bis-porphyrin-substituted phthalonitrile **51** to its diiminoisoindoline derivative followed by cyclization in the presence of $Zn(OAc)_2{\cdot}2H_2O$ and DBU in 1-pentanol. The overall photophysical properties of this nonamer resemble those of the triad **47** with a somewhat lower triplet quantum yield ($\Phi_T = 0.04$ versus $\Phi_T = 0.10$), shorter triplet lifetime ($\tau_T = 170\ \mu s$ versus $\tau_T = 260\ \mu s$), but higher energy transfer efficiency ($\Phi_{ET}^{SS} = 0.95$ versus $\Phi_{ET}^{SS} = 0.77$).

3. Face-to-face aggregates held by electrostatic interactions

In addition to covalent bonding, electrostatic interaction is another common linkage to hold these macrocycles in a face-to-face manner. The early works of this class of hetero-arrays up to 1996 have been reviewed [14]. Therefore, in this section, only the recent works not mentioned in that review will be described.

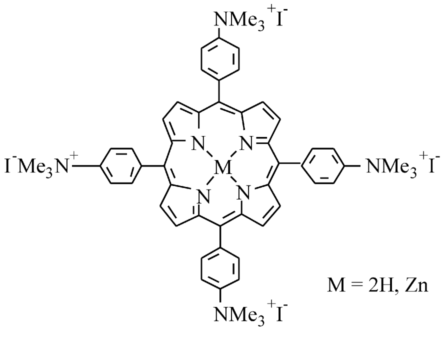
Xu and co-workers studied the self-assembly of several pairs of porphyrin and phthalocyanine bearing oppositely charged substituents. The tetra-cationic porphyrins **73** bind to the tetra-anionic phthalocyanine **74** (Plate 10) in water and other polar solvents in 1:1 stoichiometry as shown by UV–vis spectroscopy



67 **68** **66**

Scheme 11. Preparation of tetra-porphyrin-substituted phthalocyanines **66**.

and fluorescence spectroscopic titration [40]. The resulting UV–vis spectra show greatly depleted and red-shifted porphyrin Soret band and phthalocyanine Q band compared with the sum of the spectra of individual components. This observation clearly indicates that the two chromophores interact in the ground state through the electrostatic interactions between the oppositely charged substituents and the π–π interactions of the macrocycles. These hetero dimeric aggregates exhibit high stability with equilibrium formation constants in the range of $(1.2–8.9) \times 10^{8}\ M^{-1}$.



73

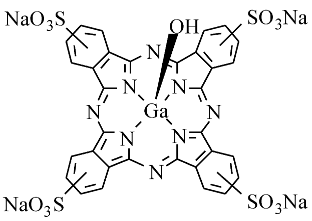


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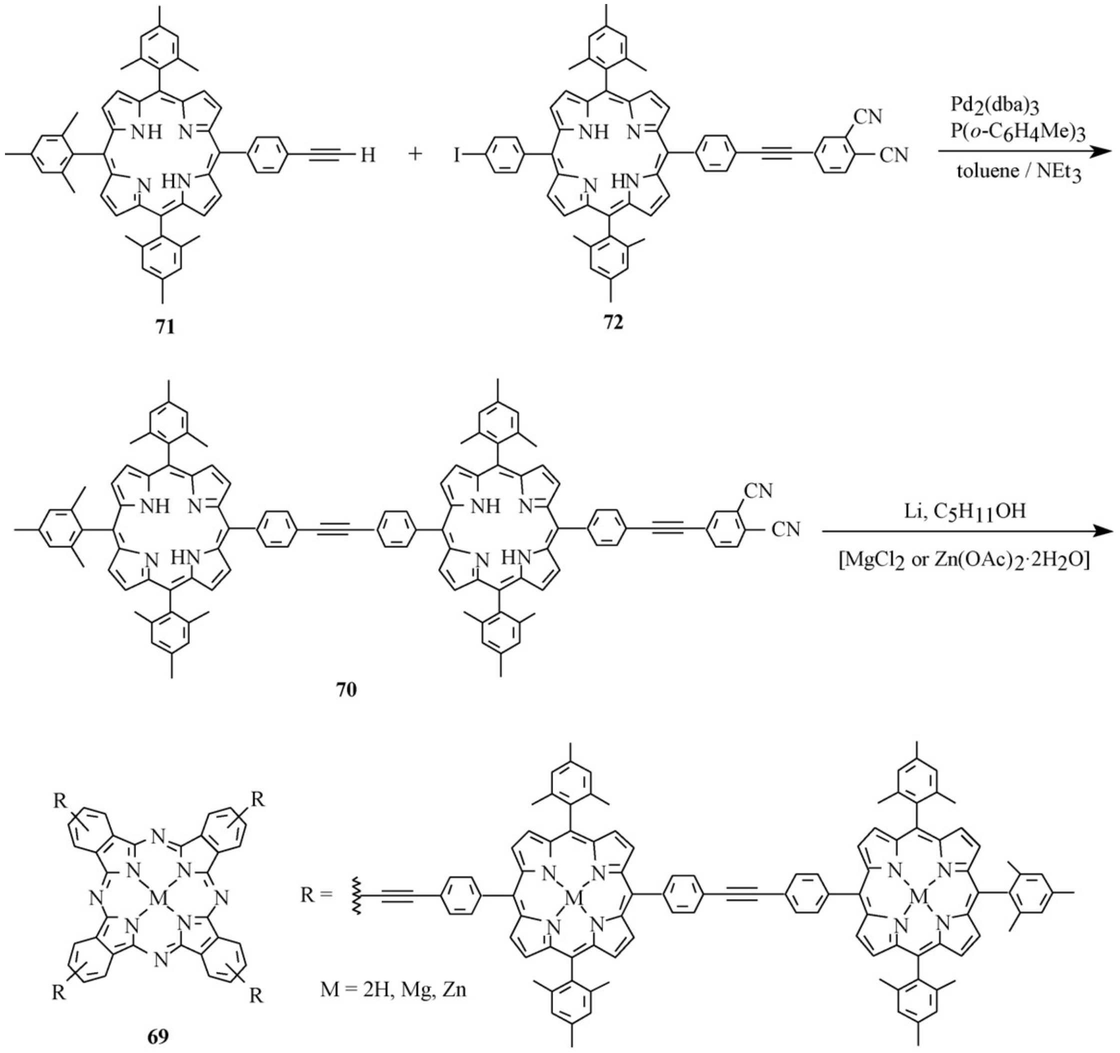
Plate 10. Structures of cationic porphyrins **73** and anionic phthalocyanine **74**.



Scheme 12. Preparation of mixed porphyrin–phthalocyanine nonamers **69**.

Similarly, the anionic sulfonated porphyrins **75** also form self-assembled face-to-face structures with the cationic phthalocyanines **76** (Plate 11) [41]. The stoichiometry (1:1 or 1:2) depends on the affinity of the metal center of these macrocycles for axially bound coordinating solvent molecules. The two chromophores in the mixed arrays exhibit a mutual quenching of the fluorescence through electron transfer as shown by the transient absorptions of the porphyrin radical cation (around 600–650 nm) and phthalocyanine radical anion (around 550–600 nm) upon nanosecond laser photolysis. The formation of a related dyad from **75** (M = 2H) and the dicationic phthalocyanine **77** (Plate 11) has also been briefly reported [42].

The self-assembly of these oppositely charged macrocycles can be extended to form multilayer films. By alternating deposition of the cobalt analogues of **73** and **74** onto an ionic substrate, a new type of functional multilayer film can be prepared [43]. The

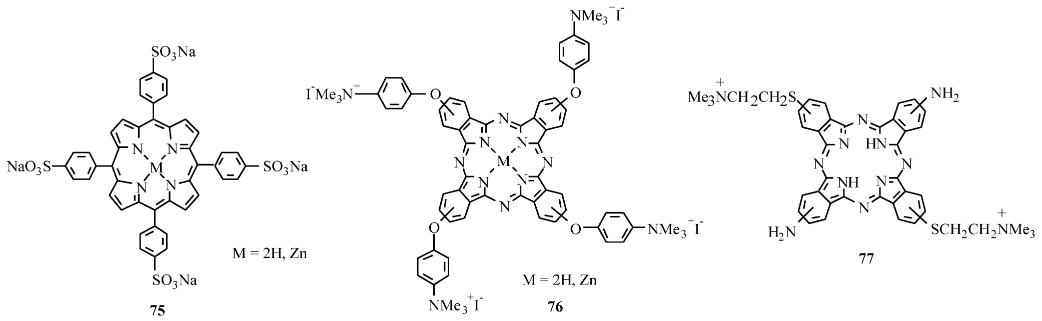


Plate 11. Structures of anionic porphyrins **75** and cationic phthalocyanines **76** and **77**.

absorption spectrum of the film shows the porphyrin Soret band and phthalocyanine Q band at 440 and 676 nm, respectively. These absorptions are red-shifted by ca. 500 and 200 cm^{-1}, respectively, compared to those in the solution spectra as a result of aggregation of chromophores within the layer. The absorbances of these two bands also increase linearly with the number of layers, showing that the consecutive absorption is uniform and regular.

Self-assembled amphiphilic dyads can also be used to form Langmuir–Blodgett (LB) films. By alternating deposition of fatty acids and the hetero-dyad of zinc(II) *meso*-tetrakis(4-*N*-doeicosylpyridinium)porphyrin and copper(II) tetrasulfonated phthalocyanine, LB multilayers are formed [44]. Upon excitation of the porphyrin ring, long-lived radical ions are formed in the layers, while energy transfer is observed in solution. The difference in behavior can be attributed to the local high polarity experienced by the dyad in the former medium.

Similarly, LB films can also be fabricated using the amphiphilic zinc(II) β-tetrakis[(4-*N*,*N*-dimethyl-*N*-octadecylammonium)phenoxy]phthalocyanine and *meso*-tetra(*p*-tolyl)porphyrin [45]. A monolayer of these two compounds can be spread on water from chloroform solution and transferred onto CaF_2 slides. According to the surface pressure–area isotherms and UV–vis spectroscopic studies, it can be concluded that the porphyrin ring is situated in the cavity between the long alkyl chains of phthalocyanine in one layer of the LB film, and the latter macrocycle lies nearly parallel to the substrate surface.

Tran-Thi and co-workers also studied the bimolecular aggregate generated from the tetrachloride salt of the cobalt(II) *meso*-tetrakis(4-*N*-methylpyridinium)porphyrin and the aluminium analogue of **74** in DMSO [46]. Its formation constant, as determined by UV–vis spectroscopic measurements, is in the range of 10^6–10^7 M^{-1}. The complex exhibits a charge transfer character in the ground state in which the phthalocyanine ring acts as an electron acceptor. It also reversibly binds to molecular oxygen, probably through the cobalt center, to form a stable zwitterionic species. Upon excitation, the molecular oxygen is ejected and the complex relaxes to the ground state via the triplet excited state. The latter species then triggers the formation of singlet oxygen, which can be revealed by steady-state and time-resolved spectroscopic methods. Preliminary in vitro studies show that the zwitterionic species is less effective than the phthalocyanine component in photo-inactivation of EMT-6 mouse mammary tumor cells.

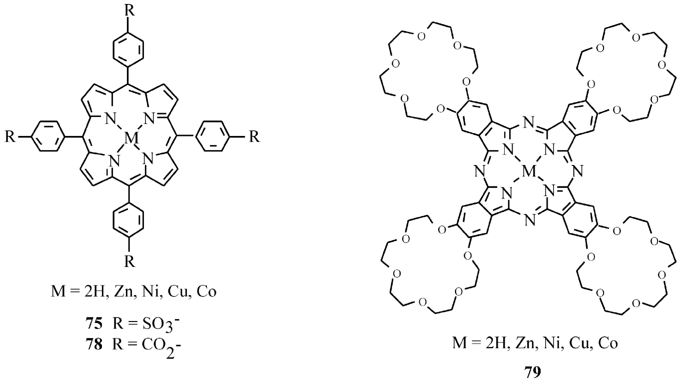
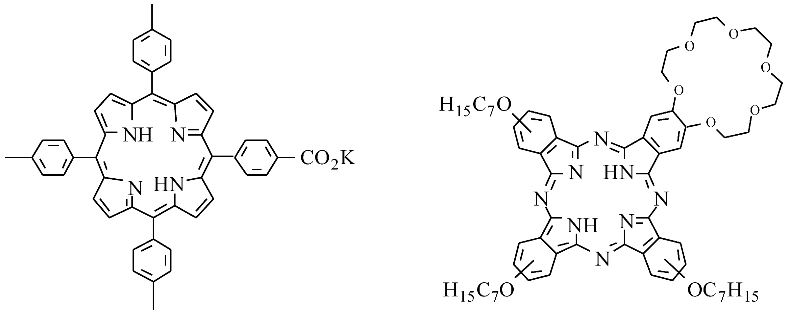


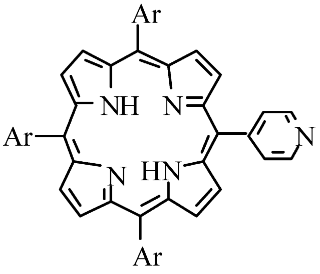
Plate 12. Structures of anionic porphyrins **75** and **78**, and tetrakis(18-crown-6) fused phthalocyanines **79**.

Rodgers et al. also examined the complexation of a series of *meso*-tetraarylporphyrins with four 4-sulfophenyl or 4-carboxyphenyl substituents at the meso positions with phthalocyanines fused with four 18-crown-6 moieties (Plate 12) [47,48]. In the presence of a potassium salt in DMSO or ethanol, the potassium ions are trapped inside the crown ethers, which are then bound to the anionic groups of porphyrin by electrostatic interactions to form 1:1 or 1:2 face-to-face mixed tetrapyrrole complexes. The UV–vis spectra are significantly changed upon complexation. Typically, the porphyrin Soret band is slightly blue-shifted and the phthalocyanine Q band vanishes with concomitant appearance of a new band in the red spectral region (ca. 700 nm). These spectral changes indicate strong electronic coupling between the chromophores. Results from spectroelectrochemical studies suggest that the complexes possess a significant charge transfer character in the ground state in which the phthalocyanine serves as an electron donor. The energy of the charge transfer state of the both-metal-free complex was estimated to be 1.70 eV which has a lifetime of 3.65 ns. Femtosecond transient absorption spectroscopy was also used to study the deactivation pathways after photoexcitation of these complexes [48]. Excitation at 400 nm populates the charge transfer state, which deactivates to form the metal-centered (d, d) state within 2 ps. The latter state repopulates the ground state with a lifetime of 7–200 ps depending on the metal center of the macrocycles.

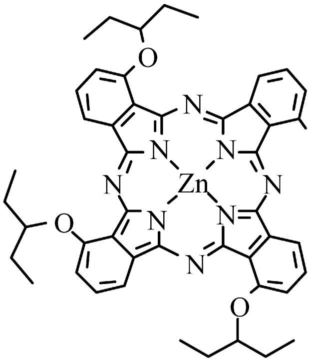


80 **81**

Plate 13. Structures of anionic porphyrin **80** and mono(18-crown-6) fused phthalocyanine **81.**



82 Ar = C_5H_4N
83 Ar = C_6H_5



84

Plate 14. Structures of pyridyl porphyrins **82** and **83**, and zinc(II) phthalocyanine **84**.

Similarly, a mixed supramolecular dyad is formed from the mono-carboxylated porphyrin **80** and the mono crown ether substituted phthalocyanine **81** (Plate 13) in chloroform [49]. This dyad can be fabricated into highly ordered LB films as shown by polarized absorption spectroscopy and low angle X-ray diffraction method. As expected, the fluorescence of porphyrin is quenched completely by the phthalocyanine in the mixed film.

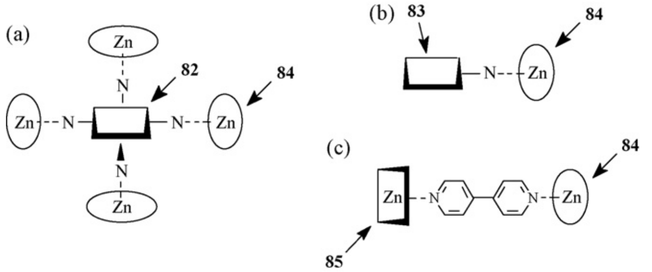
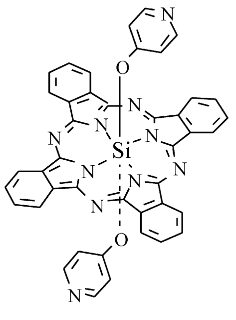


Fig. 2. Schematic diagrams showing the structures of hetero porphyrin–phthalocyanine arrays held by axial coordination.

4. Hetero-arrays held by axial coordination

Although axial coordination of metallo-porphyrins and phthalocyanines has been well documented, the use of this methodology to construct hetero-arrays of these chromophores remains little studied. Ng and co-workers first reported the self-assembly of *meso*-pyridylporphyrins **82** and **83** and zinc(II) 1,8,15,22-tetrakis(3-pentyloxy)phthalocyanine (**84**) (Plate 14) [50]. As shown by ^{1}H NMR spectroscopy and fluorescence quenching experiments, these tetrapyrrole derivatives are held by axial ligation to form edge-to-face arrays as shown in Fig. 2(a) and (b). Upon addition of **84**, the UV–vis spectrum of **82** in chloroform remains essentially unchanged, indicating that the ground-state π–π interactions between the perpendicularly disposed macrocycles are insignificant. The formation of a face-to-face hetero-dyad by the axial coordination of **84** and zinc(II) *meso*-tetra(*p*-tolyl)porphyrin (**85**) with 4,4′-bipyridine (Fig. 2(c)) is also inferred by comparing the rate of fluorescence quenching of porphyrin **85** by phthalocyanine **84** in the presence and absence of 4,4′-bipyridine.

This approach has also been extended using bis(4-pyridinolato) silicon(IV) phthalocyanine (**86**) as the core, which can axially bind to a series of zinc(II) tetrapyrrole derivatives (Plate 15) [51]. The complexation of **86** with zinc(II) *meso*-tetraphenylporphyrin (**87**) is shown by the upfield shift of all the phthalocyanine and porphyrin ring ^{1}H NMR signals as a result of the ring current generated by the coordinated partner. The signals for the pyridyl protons are also broadened due to extensive exchange between the coordinated and the free pyridyl groups. The corresponding Job's plot clearly shows a 1:2 stoichiometry, suggesting the formation of the hetero-triad (**86**)·(**87**)$_2$. The molecular structure of this novel complex (Fig. 3) has also been determined by X-ray diffraction analysis.



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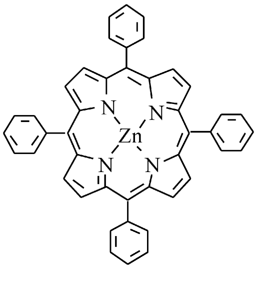

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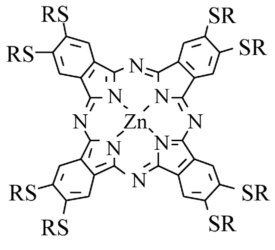


88 R = Ph
89 R = ^{n}Bu

Plate 15. Structures of pyridyl phthalocyanine **86** and zinc(II) tetrapyrrole derivatives **87**–**89**.

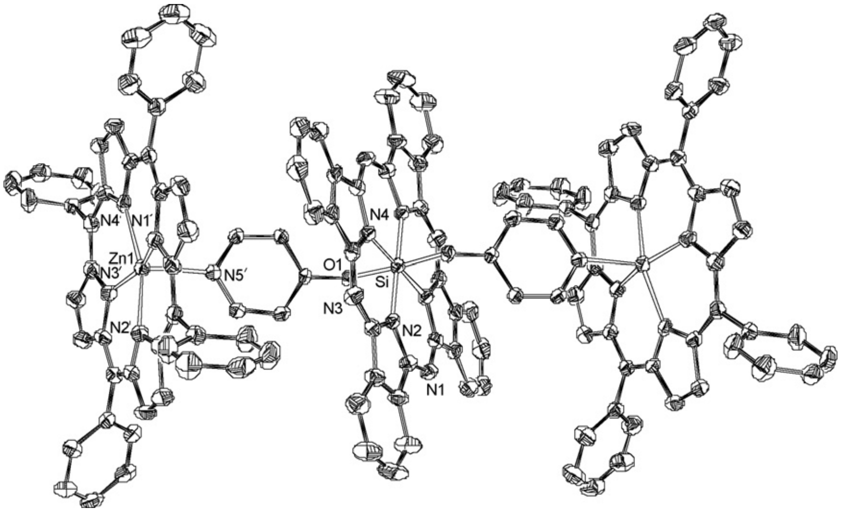
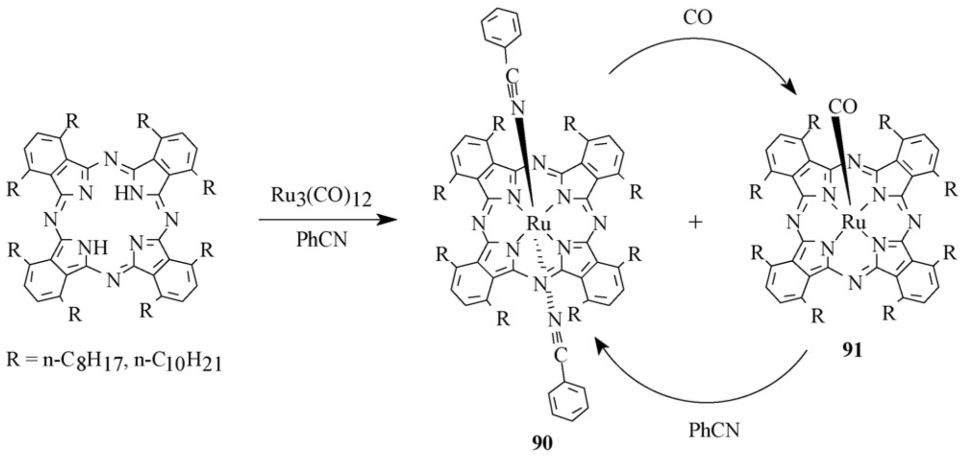


Fig. 3. Molecular structure of (**86**)·(**87**)$_2$.



Scheme 13. Preparation of ruthenium(II) phthalocyanines **90** and **91**.

The complexation of **86** with zinc(II) octathiophenoxy or octathiobutoxyphthalocyanine (**88** or **89**) has also been studied by ^{1}H NMR spectroscopy. In contrast to the complexation with porphyrin **87**, the binding is in 1:1 manner, presumably with an alternating polymeric structure in which each zinc center binds to two pyridyl groups from two molecules of **86**. The binding constants [270 M^{-1} (for **88**) and 390 M^{-1} (for **89**)] are about one order of magnitude smaller than the typical values for axial coordination of zinc(II) porphyrins with pyridine.

Cook and co-workers prepared the ruthenium(II) phthalocyanines **90** and **91** by metallation of the corresponding metal-free analogue with $Ru_3(CO)_{12}$ in refluxing benzonitrile [52,53]. The formation of these two complexes can be controlled by changing the experimental conditions as shown in Scheme 13. These ruthenium(II) phthalocyanines bind to various pyridyl ligands and can serve as useful building blocks for the construction of mixed porphyrin–phthalocyanine supramolecular arrays. For example, compound **90** binds with 2 equiv. of monopyridyl porphyrin **83** to form the triad **92** in 70% yield, while the reaction of **91** with half equiv. of dipyridyl porphyrin **93** affords the triad **94** in 65% yield (Scheme 14). Both hetero-arrays can be isolated by flash chromatography and reprecipitation. Spectroscopic studies show that there is little ground-state interaction between the chromophores in these arrays.

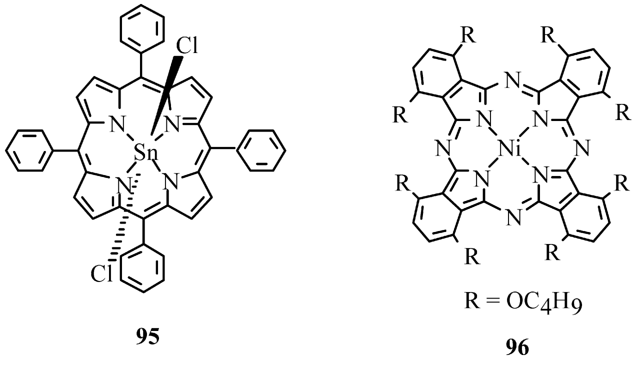
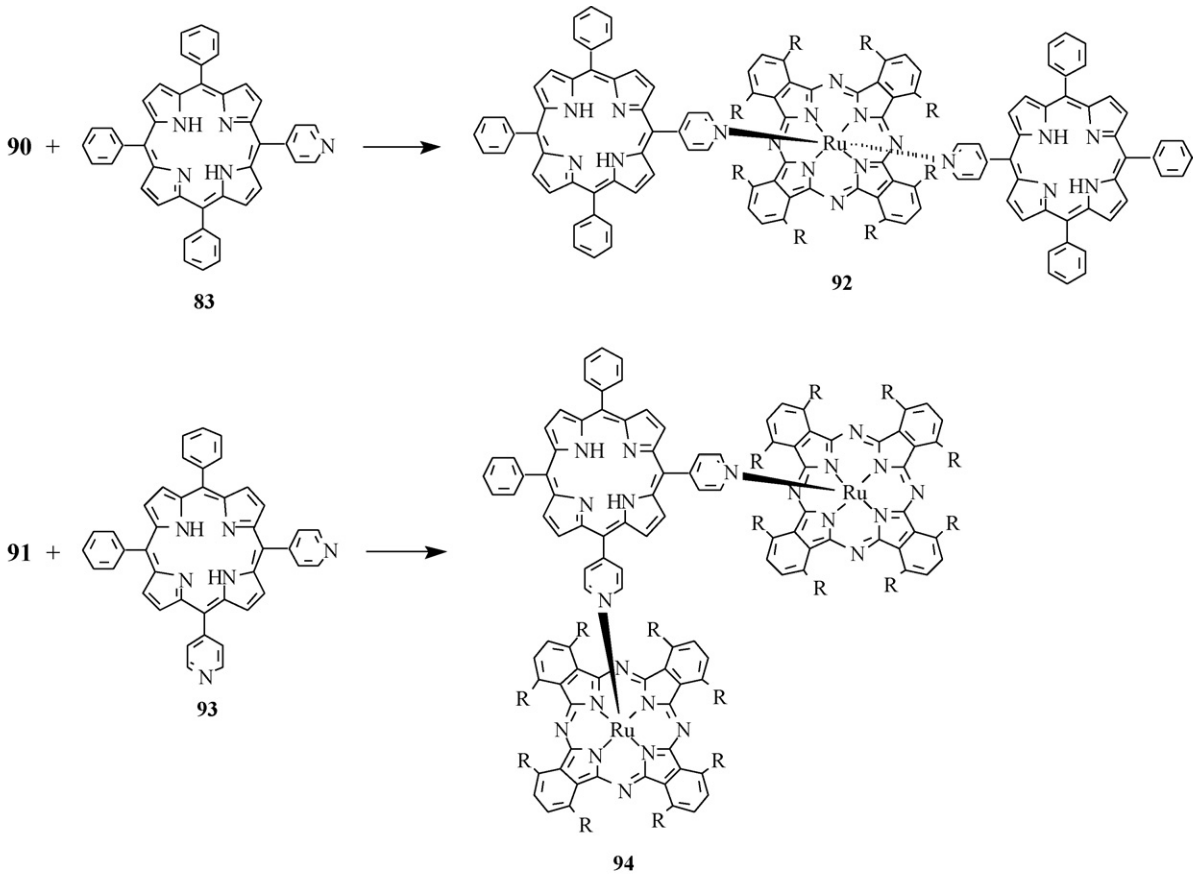


Plate 16. Structures of tin(IV) porphyrin dichloride **95** and nickel(II) phthalocyanine **96**.



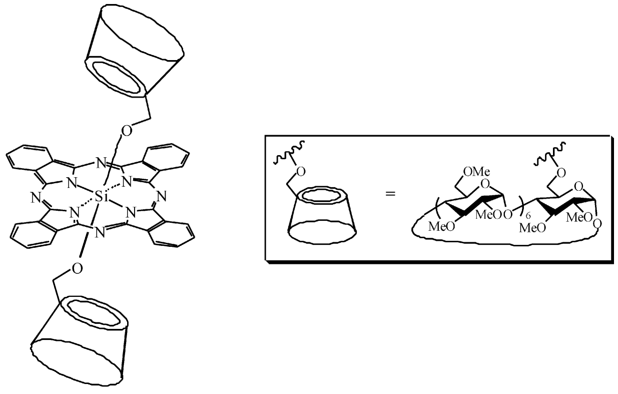
Scheme 14. Preparation of axially bound porphyrin–phthalocyanine triads **92** and **94**.

A related alternating porphyrin–phthalocyanine array has also been generated by mixing tin(IV) porphyrin dichloride **95** and nickel(II) phthalocyanine **96** in dichloromethane (Plate 16) [54]. It is believed that the macrocycles are linked through a bridging chloro ligand. In the UV–vis spectrum of the mixed array in dichloromethane, the phthalocyanine Q band at 744 nm decreases in intensity and a new band at 844 nm emerges, which may be associated with charge transfer interaction through Sn–Cl–Ni bonding rather than π–π facial interaction. The Ni K-edge X-ray absorption near edge structure (XANES) study has shown that the nickel center changes from a square planar environment to an octahedral structure upon addition of **95**, which supports the axial ligation of nickel to the chloro ligand. There is also a higher-energy shift (0.2 eV) of the preedge peak indicating that nickel is partially oxidized by charge transfer in the array.

5. Hetero-arrays held by host–guest interactions

Apart from electrostatic interactions and axial coordination, host–guest interactions have also been employed recently to assemble a mixed porphyrin–phthalocyanine array [55]. The system involves the silicon(IV) phthalocyanine **97**, which has two permethylated β-cyclodextrin units as the axial ligands (Plate 17), and the tetrasulfonated porphyrin **75** (M = 2H). The former can be prepared in 42% yield by treating silicon(IV) phthalocyanine dichloride with mono-6-hydroxy permethylated β-cyclodextrin and NaH in toluene. The host molecule binds strongly with the porphyrin guest in water. Both absorption and fluorescence spectroscopic studies show that the binding is in 1:1 manner, presumably forming a head-to-tail polymeric structure (Fig. 4). The complex stability constant is in the order of $10^8\ M^{-1}$. The encapsulation of **75** (M = 2H) into the cavity of the β-cyclodextrin of **97** is also supported by 2D ROESY experiments.

Upon excitation at 510 nm, where only the porphyrin has a weak absorption, the 1:1 host–guest complex in water gives



97

Plate 17. Structure of cyclodextrin-conjugated phthalocyanine **97**.

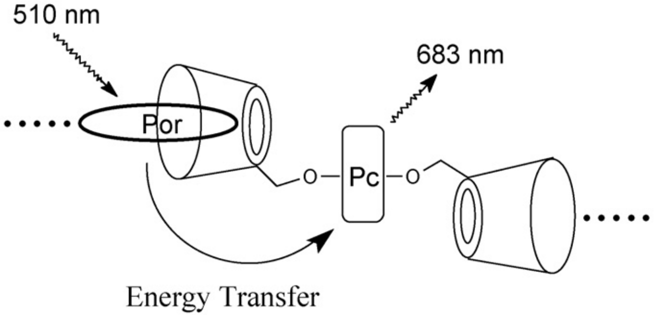


Fig. 4. Schematic diagram showing the head-to-tail polymeric structure of the host–guest complex of **97** and **95** (M = 2H), and its energy transfer property.

a strong phthalocyanine emission at 683 nm together with a weak residual porphyrin emission at 639 nm. This indicates the presence of an efficient singlet–singlet energy transfer process (Fig. 4), which is confirmed by excitation spectroscopy. The energy transfer quantum yield has been estimated to be 47% by comparing the normalized absorption and excitation spectra at the porphyrin's Soret band region.

In addition to the light-harvesting property, this host–guest complex has also found application in photodynamic therapy. The photocytotoxicity of this complex in water against HT29 human colon adenocarcinoma cells is virtually the same as that of phthalocyanine **97** itself formulated with Cremophor EL. The respective 50% growth-inhibitory ratio (IC_{50}) values are 0.09 and 0.15 μM, showing that both systems are highly photocytotoxic. The use of this supramolecular approach can prevent the use of Cremophor EL, which may cause serious hypersensitivity reactions.

6. Concluding remarks

A substantial number of hetero-arrays of porphyrins and phthalocyanines have been constructed over the last two decades. Due to the complementary absorptions of these chromophores and their distinct electrochemical and photophysical characteristics, these mixed tetrapyrrole hybrids not only serve as excellent models for the study of various photo-induced processes, but also find potential applications in artificial photosynthesis, optoelectronics, and photodynamic therapy, etc. Apart from the traditional linkages such as covalent bonding, metal complexation to form sandwich-type complexes, and electrostatic interactions to generate face-to-face aggregates, supramolecular chemistry is another strategy to link up these tetrapyrrole derivatives. This approach is in fact of particular interest and importance due to its versatility and facile preparation procedure. Supramolecular assemblies of these macrocycles, however, remain little studied. To date, only a few mixed porphyrin and phthalocyanine arrays held either by axial coordination or host–guest interactions have been reported. To our knowledge, hetero-arrays linked by hydrogen bonds or other supramolecular interactions remain unknown so far. It is envisaged that this kind of supramolecular arrays will be one of the future research focuses. We hope this article will stimulate further research on this novel class of functional dyes.

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