Convenient Synthetic Route to Rigid Donor−{Bridge}−Acceptor Systems Involving Porphyrin and Phenanthroline Annulation of Norbornylogous Bridges *via* 2,3-Norbornanediones

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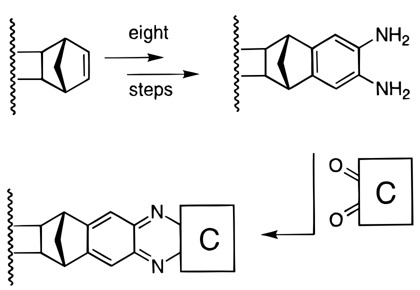
Important to the rational design and understanding of the photophysical properties of photosynthetic mimics is the preparation of rigid covalently-linked multichromophoric systems in which interchromophore separations and orientations are well-defined.[1−6] Over the past 11 years, we have been designing and synthesizing multichromophoric systems using the highly rigid hybrid norbornane−bicyclo[2.2.0]hexane bridge for the purpose of studying through-bond-mediated electron-transfer (ET) and energy-transfer (EnT) processes. This work has provided important insight into how the dynamics of ET and EnT depend on such crucial characteristics as bridge length and configuration.[2−5] An advantage of our approach has been the ability to append a wide variety of chromophores to the termini of the bridge.[2a] One method of attachment[4,6] employed by us is depicted in Scheme 1 and entails an eight-step process by which a norbornene derivative is annulated with a 1,2-diaminobenzene unit. Condensation of the diamine with a porphyrin-2,3-dione[7] or with 1,10-phenanthroline-5,6-quinone gives rise to suitable bichromophoric systems. The length of the synthetic strategy, combined with the norbornylogous bridge-building process, makes this a somewhat inefficient and tedious method for providing large quantities of materials for study. In this paper, we wish to describe a much shorter and efficient approach to the attachment of porphyrin and phenanthroline ligands to norbornylogous bridges, which may also permit sensitive functionalities elsewhere. This approach not only provides us with a new basis set for studying ET and EnT processes but also introduces a new family of dinucleating ligands of the type **3**. Figure 1 illustrates a few of the bichromophoric systems that have been prepared by this approach.

Scheme 1



The conversion of a norbornene unit to the corresponding bichromophore, *via* an α-dicarbonylnorbornane, is outlined in the Table 1. Norbornene derivatives **5**−**9** can be catalytically *cis*-dihydroxylated using OsO$_4$ catalyst and either the NMO[8] or the Et$_4$NOAc/*t*-BuOOH[9] procedure. We chose the former method since the latter was prone to acetonide formation. The NMO method suffered little from any shortfalls and can be used efficiently on a 2−5 g scale. Even compound **8**, which contains a sterically encumbered olefin, underwent the dihydroxylation in good yield (Table 1). 4-Acetamido-TEMPO[10] was the reagent of choice for the oxidation of the diols **10**−**13** to the respective diones **15**−**18**, since the standard oxidation procedures[11−14] gave low conversion by either effecting ring cleavage[13] or electrophilic substitution reaction[11−14] at the aromatic ring in the case of **10** and **11**. Condensation of the diones **15**−**18** with 1,2-diamines such as the 1:1 adduct formed between benzenetetramine[15] and a porphyrin−2,3-dione[16] or by using phenanthroline-5,6-diamine[17] gave the corresponding bichromophores in unoptimized 60−80% yield. For the the porphyrin-containing systems, demethylation (BBr$_3$, CH$_2$Cl$_2$) of the aromatic methoxy groups followed by oxidation (PbO$_2$, CHCl$_3$) gave the porphyrin−bridge−quinone systems **1a,b** (see Figure 1) in high (>90%) yield. In a similar fashion, the

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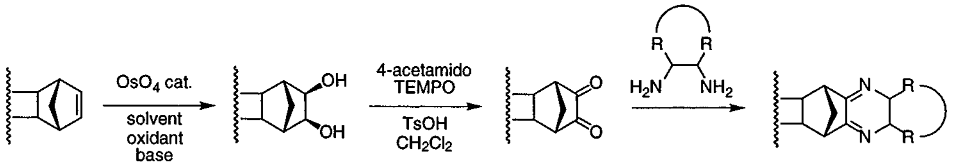
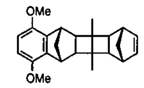
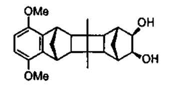
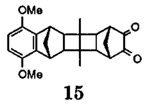
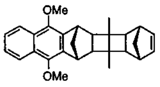
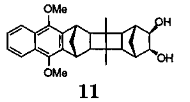
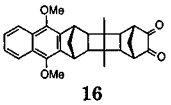
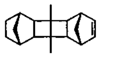
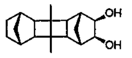
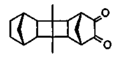
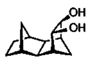
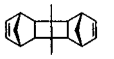
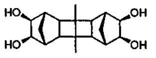
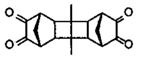
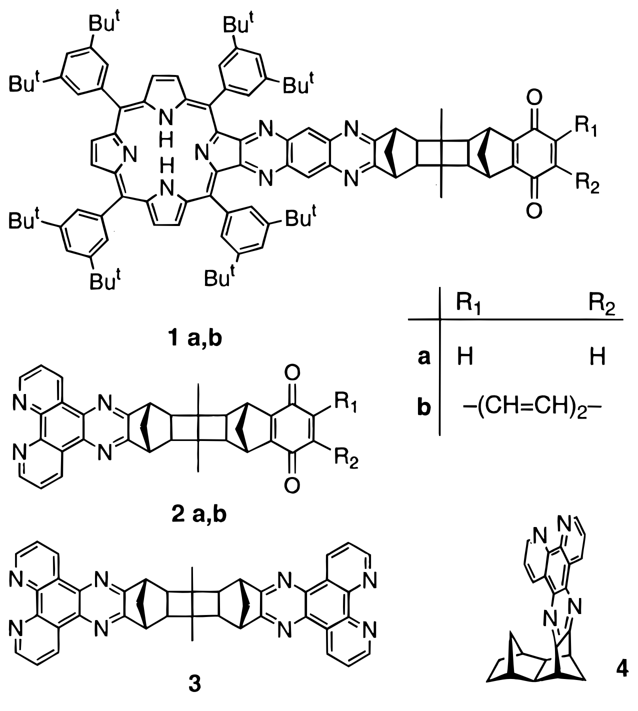
Table 1. Optimization for Dihydroxylation of Norbornene Derivatives and Their Oxidation with 4-Acetamido-TEMPO



entry	substrate	diol product	yield[a] (%)	dione product	yield[a] (%)	final compound	yield[a,e] (%)
1	 5	 10	85[b]	 15	59	**1a**	54
2			80[c]			**2a**	32
3	 6	 11	78[b]	 16	71	**1b**	75
4			79[c]			**2b**	46
6	 7	 12	53[c]	 17	56	**20**	79
						21	85
7	 8	 13	60[c]	 18	75	**4**	50
8	 9	 14	68[c]	 19	28[d]	**3**	52

[a] Yields are for isolated products. [b] Et_4NOAc/*t*-BuOOH method. [c] NMO method. [d] Synthesized by SO_3.py method. [e] Yield from dione or tetraone to final structure.



	R_1	R_2
a	H	H
b	–(CH=CH)$_2$–	

Figure 1.

phenanthroline–bridge–quinone systems **2a,b** (see Figure 1) have also been synthesized. This general method for the attachment of chromophores can be extended to dienes such as **9**. The terminal double bonds of the diene **9** were bis-dihydroxylated using the NMO method, yielding the tetrol **14** in good yield. Oxidation of **14** to the corresponding tetraone **19** was best achieved using SO_3•-pyridine in DMSO solvent.[14] Condensation with phenanthroline-5,6-diamine gave the corresponding bisphenanthroline compound **3**, whose metallation and electrochemical properties will be described shortly.

In summary, we have illustrated an efficient approach to appending porphyrin and phenanthroline units to a norbornane framework. The method is flexible enough to encompass different bridge sizes and configurations.[2a] The porphyrin systems have been successfully transformed into the totally rigid bichromophoric systems **1a** and **1b**, which are under photophysical investigation at this time. We have also demonstrated the potential of this approach as an efficient means of attaching chromophores to "kinked" molecular structures (*e.g.*, **4**) and as an agent in making rigid dinuclear compounds (*e.g.*, **3**).[18,19]

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Supporting Information Available: Experimental procedures and characterization data for compounds **1a,b**, **3**, **4**, **10**, **11**, **15**, and **16** (3 pages).

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