Heterosupramolecular Chemistry: Synthetic Strategies for the Covalent and Noncovalent Assembly and Organization of Nanocrystals and Molecules

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Described are the preparation of nanocrystals and the synthesis of molecules that may be covalently or noncovalently assembled in solution to yield heterosupermolecules possessing a well-defined heterosupramolecular function. Also described are preparative and synthetic methods that yield organized assemblies of heterosupermolecules possessing an addressable heterosupramolecular function. Finally, the development of these synthetic strategies to permit the covalent and noncovalent assembly and organization of a wide range of condensed phase and molecular components is outlined.

1. Introduction. – Conventionally, a supermolecule is distinguished from a large molecule as follows [1]: Firstly, the molecular components of a supermolecule are noncovalently linked; secondly, the intrinsic properties of these molecular components largely persist; and thirdly, the properties of a supermolecule are not a simple superposition of the properties of the constituent molecular components, *i.e.*, there exists a well-defined supramolecular function.

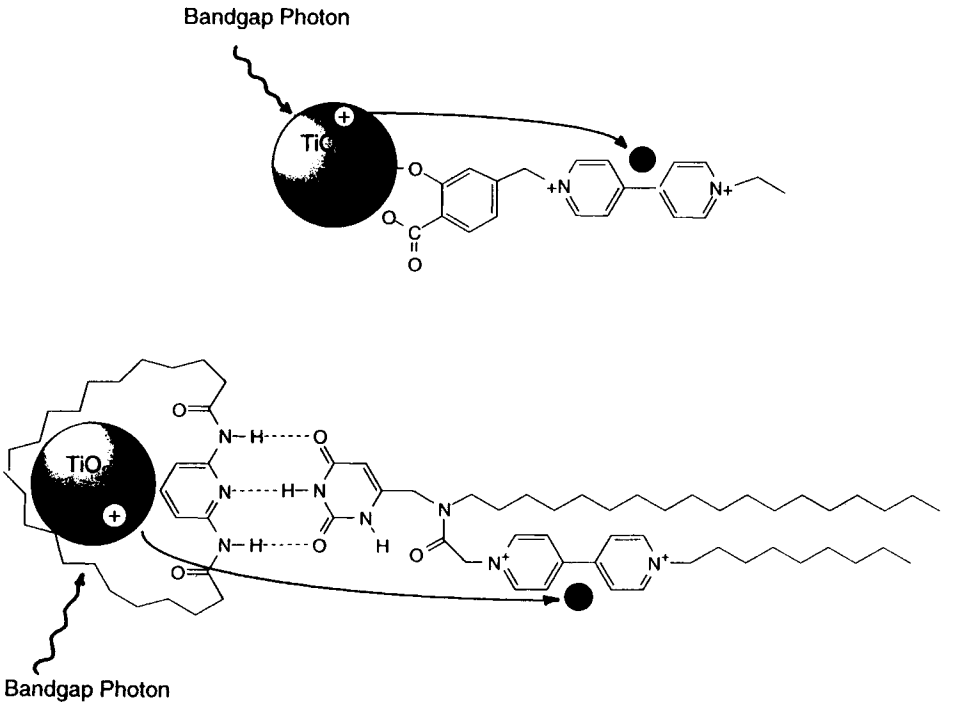
The increasingly wide-spread application of supramolecular concepts in chemistry and at the interfaces with biology and physics has, however, created the need for a more inclusive definition [2]. Consequently, the term supermolecule is increasingly applied to covalently linked molecular components provided, as above, the properties of these constituent components largely persist and there exists a supramolecular function.

A still more inclusive definition of the supermolecule has been adopted in discussing recent work directed toward the development of a chemistry of covalently and noncovalently assembled condensed phase and molecular components [3]. By analogy with a supermolecule, the properties of the constituent components of a *heterosupermolecule* largely persist, and there exists an associated *heterosupramolecular* function.

Shown in *Scheme 1* are two examples of heterosupermolecules prepared in our laboratory: They consist of a covalently or noncovalently assembled condensed phase (TiO_2 nanocrystal, electron donor) and a molecular component (viologen, electron acceptor) [4][5]. In both cases, the associated heterosupramolecular function is a light-induced vectorial electron transfer.

We now describe the preparation of nanocrystals and the synthesis of molecules that may be covalently or noncovalently assembled in solution to yield heterosupermolecules possessing a well-defined heterosupramolecular function. Also described are preparative and synthetic methods that yield organized assemblies of heterosupermolecules possessing addressable heterosupramolecular function. Finally, the development of these synthetic strategies to permit the covalent and noncovalent assembly and organization of a wide range of condensed phase and molecular components is outlined.

Scheme 1

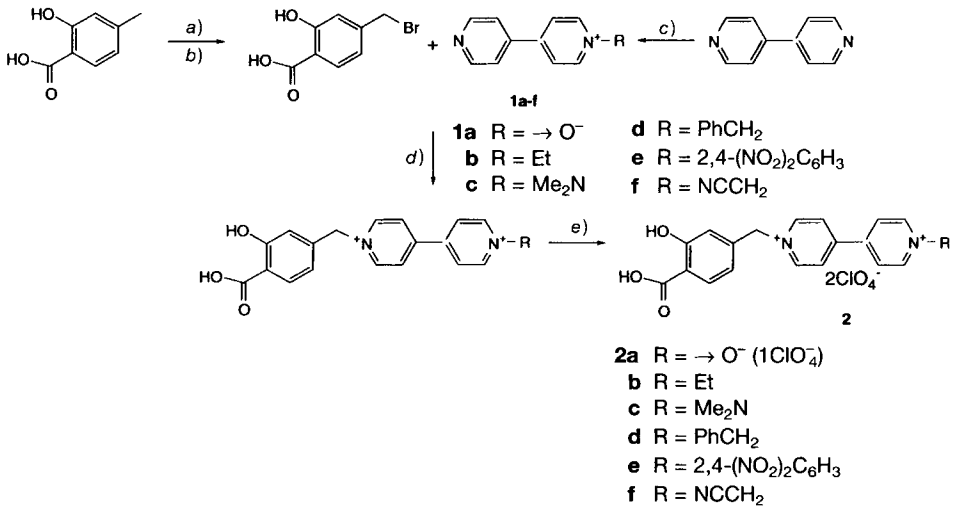


2. Results and Discussion. – 2.1. *Covalently Assembled Heterosupermolecules.* The recent past has seen the synthesis of efficient visible-light sensitizers for use in regenerative photoelectrochemical cells [6]. Specifically, ruthenium complexes containing bipyridine ligands derivatized by addition of carboxylic-acid groups have been prepared which are irreversibly adsorbed at the surface of the constituent nanocrystals of the nanostructured TiO_2 film which serves as the photoanode. It has been proposed that ligands containing such groups displace less basic solvent molecules and chelate Ti^{4+} sites at the surface of a TiO_2 nanocrystal [7].

In this context, *Moser* and *Grätzel* have studied the chemisorption of a series of model compounds at the surface of the constituent nanocrystals of a nanostructured TiO_2 film [7e]. They found salicylate (= 2-hydroxybenzoate) is strongly adsorbed at a single Ti^{4+} site and is oriented normal to the substrate surface. Chemisorption of this molecule is also accompanied by development of a visible charge-transfer absorption band [8]. Clearly, therefore, salicylate may be used to covalently assemble a TiO_2 nanocrystal and a viologen (= 4,4′-bipyridinium) molecule in solution.

Accordingly, the salicylate-containing viologen molecules **2a–f** were synthesized from **1a–f** (see *Scheme 2*) and chemisorbed at the surface of the TiO_2 nanocrystals in a stable aqueous or ethanolic colloidal dispersion at pH 3.0 [4][9]. As salicylate is adsorbed normal to the crystallite surface at a single Ti^{4+} site [7e], and as dications are not adsorbed at the positively charged surface of the TiO_2 nanocrystals at pH 3.0 [10], it may be assumed that the viologen molecule is oriented normal to the nanocrystal surface as shown in *Scheme 1*.

Scheme 2



a) MeOH/H^+. *b*) *N*-Bromosuccinimide, CCl_4. *c*) **1a**: H_2O_2, AcOH; **1b**, **d**, **f**: RX, toluene, reflux; **1e**: RX, EtOH, reflux; **1c**: from **1e** and Me_2NNH_2. *d*) MeCN reflux. *e*) 1M $HClO_4$, reflux.

Since the electron-withdrawing capacity of the terminating group R at the viologen moiety increases on going from **2a** to **2f**, the first reduction potential of these molecules is at increasingly positive potentials (see *Table*). It is noted, however, that the preparation of viologens with still more positive first reduction potentials has proved problematic [11]. Specifically, the addition of a more electron-withdrawing group at the 4′-position yielded viologens which were unstable in solution and rapidly decomposed. Further, the use of two less electron-withdrawing groups, one each at positions N(1) and N(1′), is precluded by the presence of the salicylate moiety at N(1). An alternative strategy, the introduction of electron-withdrawing groups at C(3) and C(3′) [12], yielded viologens with more positive first reduction potentials but which were deactivated with respect to addition of the salicylate moiety at either N(1) or N(1′).

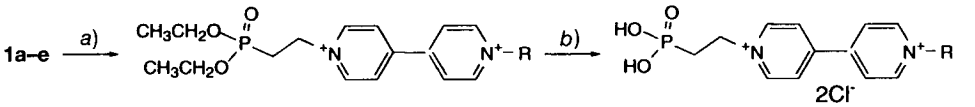
Table. *Formal Electrode Potentials*[a])

	First reduction potential [V] *vs.* SCE		
	R	**2**	**3**
a	→ O^-	−680	−0.86
b	Et	−420	−0.69
c	Me_2N	−380	−0.67
d	$PhCH_2$	−370	−0.64
e	2,4-$(NO_2)_2C_6H_3$	−350	−0.56

[a]) Measurements were performed in a buffered aqueous solution (pH 6.6): 0.1M KCl, 0.005M Na_2HPO_4, and 0.005M NaH_2PO_4. The working, counter, and reference electrodes were F-doped tin oxide conducting glass, Pt, and saturated calomel, respectively.

Recently, it has been found that ruthenium-based complexes containing bipyridine ligands derivatized by addition of phosphonic-acid groups are even more strongly chemisorbed at TiO_2 [13]. Chemisorption was, as above, discussed in terms of the displacement of less basic solvent molecules and chelation of surface Ti^{4+} sites. Accordingly, the phosphonate-containing viologens **3a–e** were synthesized as shown in *Scheme 3*. The first reduction potentials of **3a–e** are also given in the *Table*.

Scheme 3



3

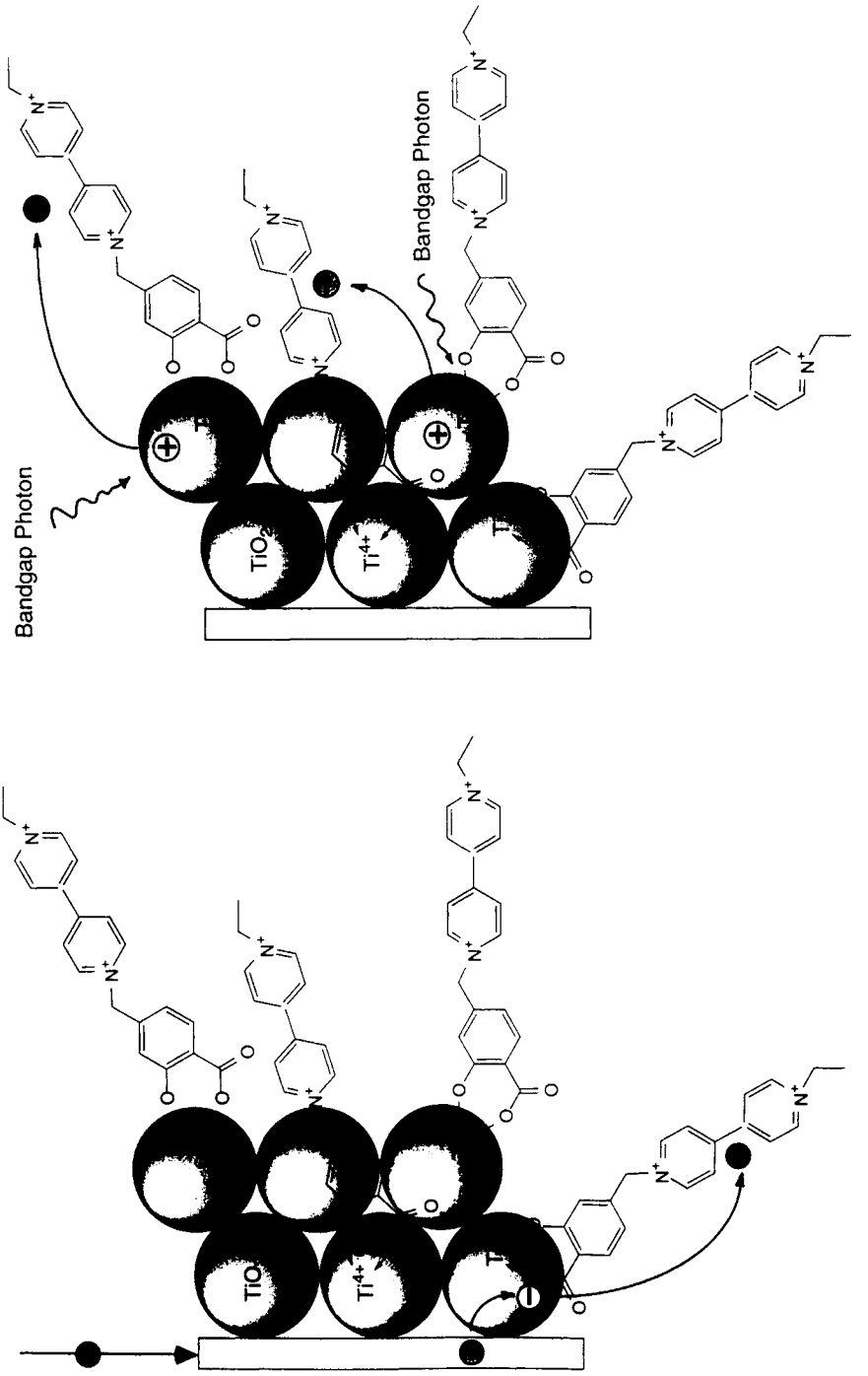
3a R = → O^- ($1Cl^-$)
b R = Et
c R = Me_2N
d R = $PhCH_2$
e R = 2,4-$(NO_2)_2C_6H_3$

a) Diethyl (2-bromoethyl)phosphonate, H_2O, reflux. *b*) 50% HCl, reflux.

The viologens **2a–f** and **3a–e** were each chemisorbed at the surface of a TiO_2 nanocrystal. Bandgap excitation of these covalently assembled heterosupermolecules resulted in electron transfer from the TiO_2 nanocrystal (electron donor) to the viologen moiety (electron acceptor), *i.e.*, light-induced vectorial electron transfer occurred [4]. As the first reduction potential of the viologen may be varied systematically, the rate of electron transfer may be determined as a function of the associated change in free-energy change [9]. Although similar studies have previously been reported [14], a unique advantage of the approach outlined above is that the separation and relative orientation of the TiO_2 nanocrystal and viologen molecule is known.

2.2. *Covalently Organized Heterosupermolecules.* The covalent assembly of a TiO_2 nanocrystal and a viologen molecule was desribed above (see *Sect. 2.1*). In a development of this approach, a viologen was chemisorbed, again using salicylic acid, to the surface of one of the constituent TiO_2 nanocrystals of a 4-μm thick nanostructured film supported on conducting glass [4][15]. It is noted that the nanocrystals of a nanostructured TiO_2 film are in ohmic contact with each other and the conducting support [16]. The resulting heterosupramolecular assembly is shown in *Scheme 4*.

At sufficiently negative applied potentials electrons occupied the conduction band of the nanostructured TiO_2 film and were subsequently transferred to the viologen molecules covalently linked to the surface of the nanocrystals (see *Scheme 4*) [4][16]. It has been shown that bandgap excitation leads to the formation of electron-hole pairs in the nanostructured TiO_2 film, and that, in the presence of a suitable hole scavenger, the photogenerated conduction-band electrons are transferred to the viologen molecules covalently linked to the surface of the nanocrystals (see *Scheme 4*) [4][15]. In the cases examined here, the associated heterosupramolecular function was light-induced electron transfer. It should be noted that the studied assemblies are not organized hetero-

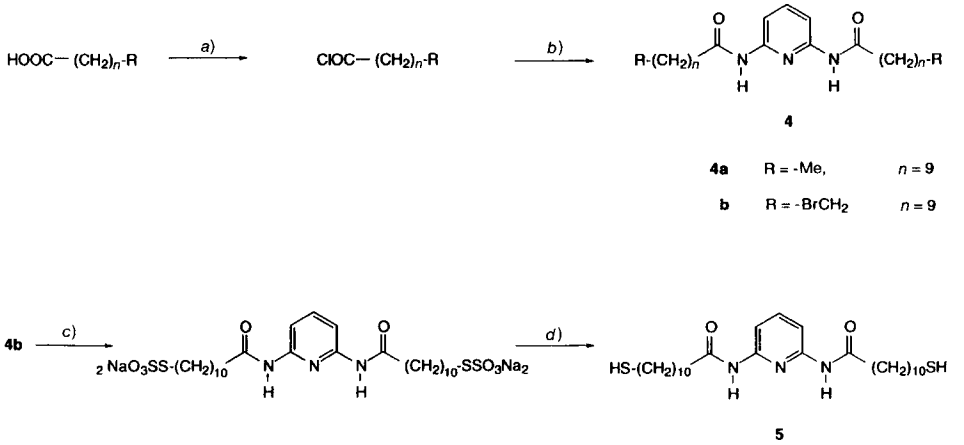


Scheme 4

supramolecular assemblies and, therefore, the constituent heterosupermolecules were not individually addressable. Moreover, the constituent heterosupermolecules did not act fully independently, *i.e.*, there was electron transfer between viologens adsorbed at the same or adjacent nanocrystals.

2.3. *Noncovalently Assembled Heterosupermolecules.* An alternative approach to the covalent assembly (*Sect. 2.1*) is the noncovalent assembly of a TiO_2 nanocrystal and a viologen molecule [5]. Toward this end, TiO_2 nanocrystals were prepared in the presence of a modified stabilizer **4a** whose synthesis is shown in *Scheme 5* [5][17][18]. This stabilizer incorporates a diaminopyridine moiety which can recognize and selectively bind a uracil moiety by complementary H-bonding [19]. (A similar stabilizer **5** was synthesized for use with gold and silver nanocrystals, see below.) Probably **4a** was physisorbed at the surface of a nanocrystal as the resulting dispersion, which otherwise flocculates on the time scale of seconds, was stable for a period of months. More quantitatively, ^{1}H-NMR studies showed that the resonances assigned to the methylene and methyl groups of **4a** were shifted and split by interaction with the surface of a TiO_2 nanocrystal.

Scheme 5

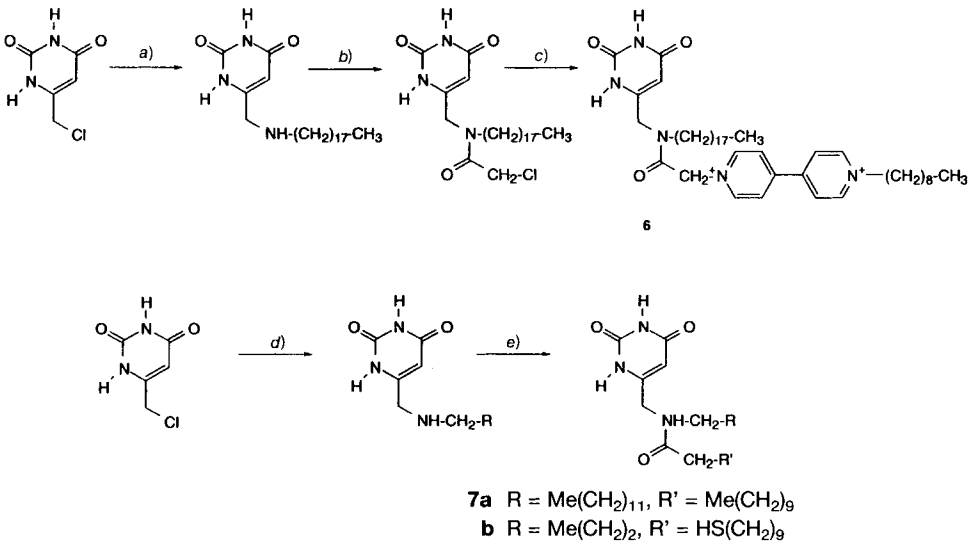


a) $SOCl_2$, reflux. *b*) Pyridine-2,6-diamine, $CHCl_3$ (added pyridine), r.t. *c*) $Na_2S_2O_3$. *d*) 1M HCl, reflux.

The synthesis of a viologen molecule **6** incorporating an uracil moiety is shown in *Scheme 6*. Viologen **6** belongs to a series of compounds of the same type which were also prepared and studied. The corresponding results revealed that viologen molecules of type **6** with much less than 25 CH_2 groups in the alkane chains were not soluble in $CHCl_3$. However, for viologen molecules with much more than *ca.* 25 CH_2 groups, micellization was observed in $CHCl_3$ at the concentrations necessary to allow characterization of the resulting heterosupramolecular complex by ^{1}H-NMR and IR. Accordingly, studies were generally performed in acetone/$CHCl_3$ 1:1 (*v*/*v*) [5].

On mixing a colloidal TiO_2 nanocrystal dispersion, prepared in the presence of the stabilizer **4a** incorporating the diaminopyridine moiety, with a solution of a viologen derivative of type **6** incorporating the uracil moiety, the former recognized and selectively

Scheme 6



a) $Me(CH_2)_{17}NH_2$, i-PrOH, reflux. *b*) $ClCH_2COCl$, $CHCl_3$ (added pyridine), r.t. *c*) 1-Nonyl-4,4'-bipyridinium chloride, MeCN, reflux. *d*) RCH_2NH_2, i-PrOH, reflux. *e*) RCH_2COCl, $CHCl_3$ (added pyridine), r.t.

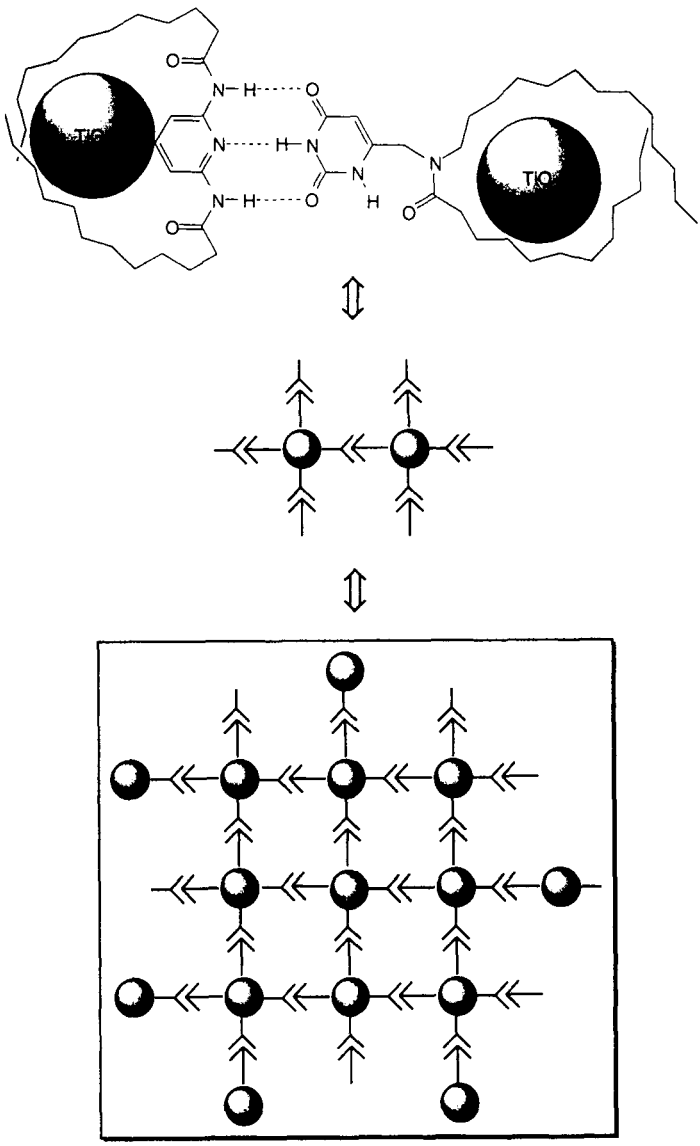
bound the latter as shown in *Scheme 1*. Bandgap excitation of a TiO_2 nanocrystal was followed by electron transfer to the noncovalently bound viologen molecule. The associated heterosupramolecular function was, therefore, a light-induced vectorial electron transfer.

Briefly, these studies were extended to permit the noncovalent assembly of two TiO_2 nanocrystals. As before, TiO_2 nanocrystals were prepared in the presence of the modified stabilizer **4a** [5][17]. However, TiO_2 nanocrystals were also prepared in the presence of the modified stabilizer **7a** incorporating the uracil moiety [5][17]. On mixing, these nanocrystals recognized and selectively bound each other as shown in *Scheme 7* [5]. Further, under appropriate conditions, these nanocrystals self-organized to form an extended array in solution [5]. Some evidence for short-range ordering of these nanocrystals was obtained.

2.4. *Noncovalently Organized Heterosupermolecules.* In a development of the studies described in *Sect. 2.3*, a noncovalently organized assembly of TiO_2 nanocrystals and viologen molecules was prepared. Thus, phosphonic acid **8** was synthesized as shown in *Scheme 8*. The long alkane chain ensures this molecule is sufficiently hydrophobic to be deposited as a close-packed monolayer using *Langmuir-Blodgett* (*LB*) techniques. The phosphonic-acid head group ensures irreversible attachment of the deposited monolayer to the constituent nanocrystals of a TiO_2 substrate [11] (see below). The viologen molecule **9** was synthesized according to *Scheme 8*. This molecule contains two alkane chains, equal in length to that in **8**, ensuring that this molecule is also sufficiently hydrophobic that it may be deposited as a close-packed monolayer using *LB* techniques.

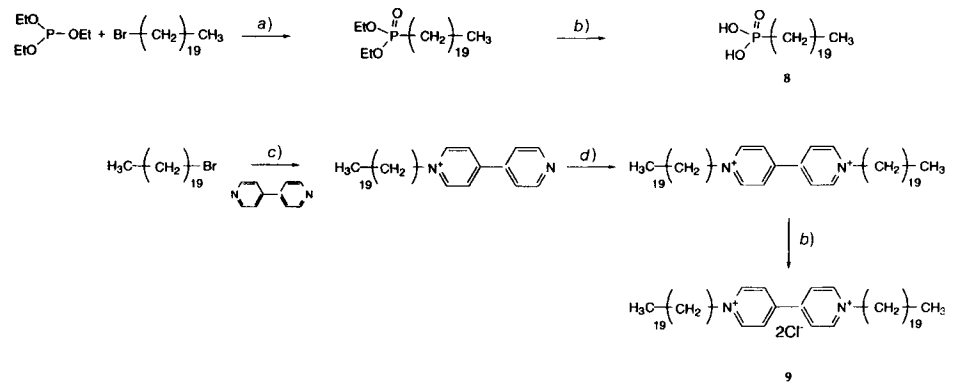
To prepare the heterosupramolecular assembly shown in *Scheme 9*, a close-packed monolayer of TiO_2 nanocrystals was first deposited, using *LB* techniques, on a conduct-

Scheme 7



ing glass substrate. A close-packed mixed monolayer of **8** and **9** (ratio 12:1) was then deposited on the nanocrystal monolayer, also by *LB* techniques. Detailed characterization confirmed that the deposited molecular monolayer has the structure shown [20]. Thus it can be stated that there is a single viologen associated with each nanocrystal, that each viologen has a well-defined orientation with respect to that nanocrystal, and that electron transfer between adjacent viologens is not observed. All of these characteristics

Scheme 8



a) Neat, reflux. *b*) 50% HCl soln., reflux. *c*) Toluene, reflux. *d*) MeCN, reflux.

represent advantages over those of the covalently linked heterosupramolecular assembly shown in *Scheme 4* [15].

Electron transfer from a TiO_2 nanocrystal to a viologen molecule were initiated by applying a negative potential to a TiO_2 nanocrystal or by bandgap excitation of the same [20]. It should be noted that in the organized heterosupramolecular assembly shown in *Scheme 9*, the constituent heterosupermolecules were addressable. Moreover, because each heterosupermolecule is isolated, the heterosupermolecules acted fully independently.

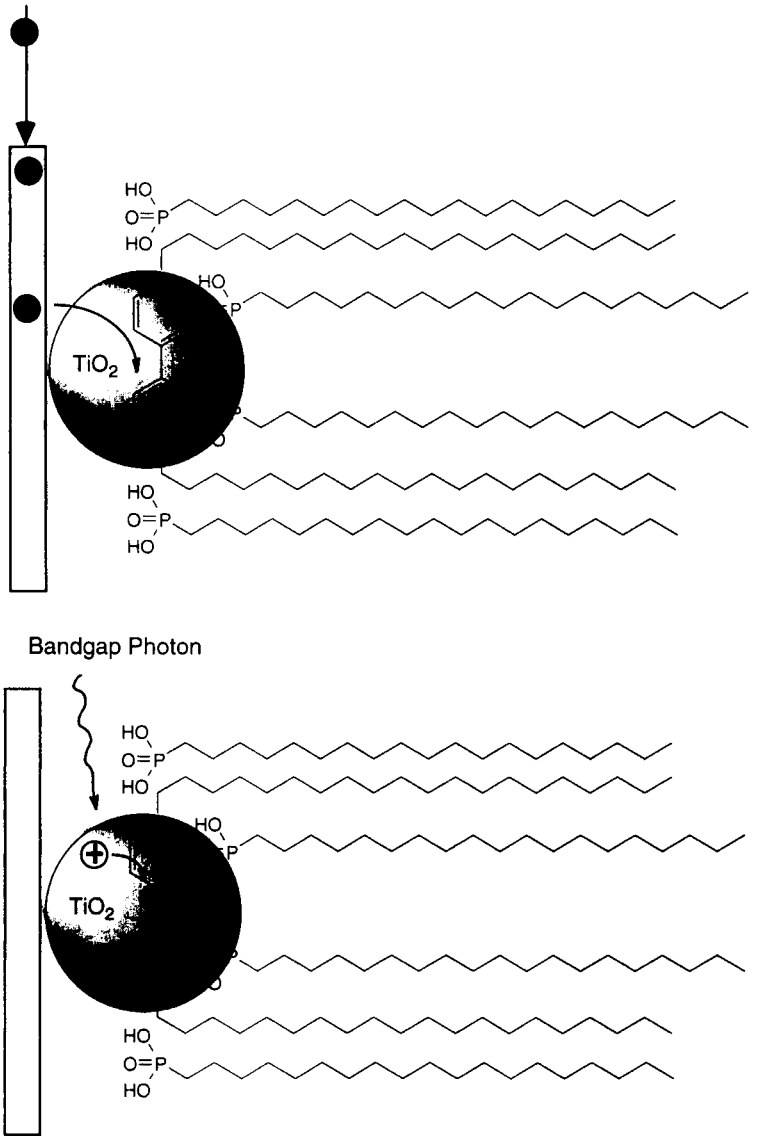
2.5. *Future Work*. Future work in this area will be directed toward the preparation and synthesis of a wider range of condensed phase and molecular components and their incorporation into heterosupermolecules and organized assemblies of heterosupermolecules possessing novel and diverse functions. Outlined below are two examples of work of this nature that is in progress.

In the first example, the stabilizers **5** and **7b**, incorporating a diaminopyridine and a uracil moiety, respectively, and incorporating at least one thiol group, were synthesized. These stabilizers were strongly chemisorbed at the surface of silver or gold nanocrystals prepared in their presence [21][22]. These nanocrystals will be expected to recognize and selectively bind each other to form a heterosupermolecule consisting of two noncovalently assembled condensed phase components, see *Scheme 10*.

The second example relates to the noncovalent assembly of heterosupermolecules in a wide range of polar solvents. Toward this end, a series of receptor-substrate pairs known to associate in polar solvents are being investigated (see also *Scheme 10*). The first, based on a crown ether ammonium cation receptor-substrate pair, can be used to self-assemble heterosupermolecules in solvents as polar as MeCN [23]. The second, based on non-self-complementary DNA oligomers, can be used to assemble heterosupermolecules in solvents as polar as H_2O [24]. Other receptor-substrate pairs are being incorporated into heterosupermolecules.

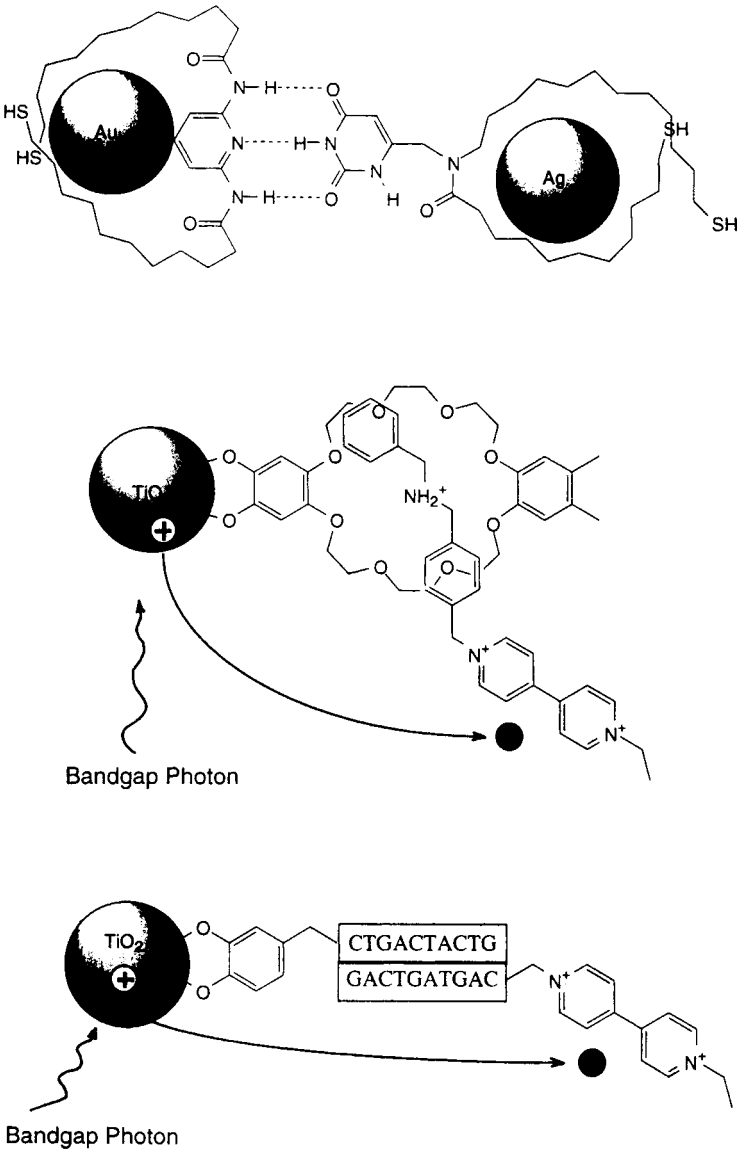
3. Conclusions. – The covalent and noncovalent assembly of condensed phase and molecular components to form heterosupermolecules possessing a well-defined hetero-

Scheme 9



supramolecular function was described, as well as the preparation of covalent and noncovalent heterosupramolecular assemblies. In both latter cases, the constituent heterosupermolecules possessed well-defined heterosupramolecular functions. In the case of the noncovalent heterosupramolecular assembly, however, the constituent heterosupermolecules were ordered and, in principle, individually addressable.

Scheme 10



Experimental Part

General. ^{1}H-NMR Spectra: δ in ppm, J in Hz. *1-[(4-Carboxy-3-hydroxyphenyl)methyl]-4,4'-bipyridinium 1'-Oxide Perchlorate* (**2a**). ^{1}H-NMR ((D_6)DMSO): 5.83 (*s*, 2 H); 7.01–7.05 (*dd*, J = 1.7, 8.1, 1 H); 7.11 (*d*, J = 1.7, 1 H); 7.81–7.84 (*d*, J = 8.1, 1 H); 8.13–8.16 (*d*, J = 7.3, 2 H); 8.43–8.46 (*d*, J = 7.3, 2 H); 8.57–8.60 (*d*, J = 7.0, 2 H); 9.22–9.24 (*d*, J = 6.7, 2 H). Anal. calc. for $C_{18}H_{15}ClN_2O_8$: C 51.14, H 3.58, N 6.63; found: C 51.24, H 3.60, N 6.54.

1-[(4-Carboxy-3-hydroxyphenyl)methyl]-1'-ethyl-4,4'-bipyridinium Diperchlorate (**2b**). ^{1}H-NMR ((D_6)-DMSO): 1.57–1.62 (*t*, *J* = 7.31, 3 H); 4.67–4.75 (*q*, *J* = 7.31, 2 H); 5.92 (*s*, 2 H); 7.07–7.11 (*dd*, *J* = 1.7, 8.16, 1 H); 7.16 (*d*, *J* = 1.7, 1 H); 7.84–7.87 (*d*, *J* = 8.16, 1 H); 8.71–8.75 (*d*, *J* = 9.29, 2 H); 8.76–8.78 (*d*, *J* = 9.29, 2 H); 9.34–9.37 (*d*, *J* = 7.0, 2 H); 9.45–9.48 (*d*, *J* = 7.0, 2 H). Anal. calc. for $C_{20}H_{20}Cl_2N_2O_{11}$: C 44.87, H 3.77, N 5.23; found: C 44.99, H 3.64, N 5.08.

1-[(4-Carboxy-3-hydroxyphenyl)methyl]-1'-(dimethylamino)-4,4'-bipyridinium Diperchlorate (**2c**). ^{1}H-NMR ((D_6)DMSO): 3.15 (*s*, 6 H); 5.92 (*s*, 2 H); 7.09–7.11 (*dd*, *J* = 1.7, 8.1, 1 H); 7.17 (*d*, *J* = 1.7, 1 H); 7.84–7.87 (*d*, *J* = 8.1, 1 H); 8.72–8.75 (*d*, *J* = 7.9, 2 H); 8.76–8.78 (*d*, *J* = 7.0, 2 H); 9.45–9.48 (*d*, *J* = 7.0, 2 H); 9.58–9.60 (*d*, *J* = 7.0, 2 H). Anal. calc. for $C_{20}H_{21}Cl_2N_3O_{11}$: C 43.50, H 3.85, N 7.64; found: C 42.45, H 4.15, N 7.23.

1-Benzyl-1'-[(4-carboxy-3-hydroxyphenyl)methyl]-4,4'-bipyridinium Diperchlorate (**2d**). ^{1}H-NMR ((D_6)-DMSO): 5.92 (*s*, 4 H); 7.06–7.09 (*dd*, *J* = 1.7, 8.1, 1 H); 7.14 (*d*, *J* = 1.7, 1 H); 7.40–7.60 (*m*, 5 arom. H); 7.83–7.86 (*d*, *J* = 8.1, 1 H); 8.71 (*d*, *J* = 1.7, 2 H); 8.73–8.74 (*d*, *J* = 1.7, 2 H); 9.45–9.47 (*d*, *J* = 5.3, 2 H); 9.47–9.49 (*d*, *J* = 5.3, 2 H). Anal. calc. for $C_{25}H_{22}Cl_2N_2O_{11}$: C 50.18, H 3.87, N 4.68; found: C 49.14, H 3.96, N 4.53.

1-[(4-Carboxy-3-hydroxyphenyl)methyl]-1'-(2,4-dinitrophenyl)-4,4'-bipyridinium Diperchlorate (**2e**). ^{1}H-NMR ((D_6)DMSO): 5.82 (*s*, 2 H); 7.07–7.11 (*dd*, *J* = 1.7, 8.1, 1 H); 7.16 (*d*, *J* = 1.7, 1 H); 7.84–7.87 (*d*, *J* = 8.1, 1 H); 8.41 (*d*, *J* = 8.8, 1 H); 8.42–8.78 (*m*, unresolved, 6 H); 9.44–9.46 (*d*, *J* = 7.0, 2 H); 9.48–9.50 (*d*, *J* = 7.0, 2 H). Anal. calc. for $C_{24}H_{18}Cl_2N_4O_{15}$: C 42.85, H 2.67, N 8.33; found: C 42.66, H 2.55, N 8.18.

1-[(4-Carboxy-3-hydroxyphenyl)methyl]-1'-(cyanomethyl)-4,4'-bipyridinium Diperchlorate (**2f**). ^{1}H-NMR ((D_6)DMSO): 5.92 (*s*, 2 H); 6.01 (*s*, 2 H); 7.07–7.11 (*dd*, *J* = 1.7, 8.1, 1 H); 7.16 (*d*, *J* = 1.6, 1 H); 7.84–7.87 (*d*, *J* = 8.1, 1 H); 8.76–8.78 (*d*, *J* = 7.0, 2 H); 8.79–8.81 (*d*, *J* = 7, 2 H); 9.44–9.46 (*d*, *J* = 7.9, 2 H); 9.48–9.50 (*d*, *J* = 7.0, 2 H). Anal. calc. for $C_{20}H_{17}Cl_2N_3O_{11}$: C 43.97, H 3.14, N 7.69; found: C 43.45, H 3.15, N 7.23.

1-(2-Phosphonoethyl)-4,4'-bipyridinium 1'-Oxide Chloride (**3a**). ^{1}H-NMR ((D_6)DMSO): 2.10–2.25 (*m*, 2 H); 4.90–5.02 (*m*, 2 H); 8.65–8.69 (*m*, 4 H); 9.12–9.23 (*m*, 4 H). Anal. calc. for $C_{12}H_{14}ClN_2O_4$: C 45.50, H 4.43, N 8.86, P 9.81, Cl 11.07; found: C 45.26, H 4.48, N 8.92, P 9.75, Cl 11.2.

1-Ethyl-1'-(2-phosphonoethyl)-4,4'-bipyridinium Dichloride (**3b**). ^{1}H-NMR ((D_6)DMSO): 1.58–1.63 (*t*, *J* = 7.33, 3 H); 2.48–2.54 (*m*, 2 H); 4.67–4.75 (*q*, *J* = 7.33, 2 H); 4.95–5.05 (*m*, 2 H); 8.87–8.93 (*m*, 4 H); 9.45–9.51 (*m*, 4 H). Anal. calc. for $C_{14}H_{19}Cl_2N_2O_3P_2$: C 46.15, H 5.21, N 7.69, P 8.51, Cl 19.23; found: C 46.10, H 5.10, N 7.52, P 8.42, Cl 19.4.

1-(Dimethylamino)-1'-(2-phosphonoethyl)-4,4'-bipyridinium Dichloride (**3c**). ^{1}H-NMR ((D_6)DMSO): 2.30–2.52 (*m*, 2 H); 3.3 (*s*, 6 H); 4.90–5.02 (*m*, 2 H); 8.64–8.76 (*m*, 4 H); 9.11–9.21 (*m*, 4 H). Anal. calc. for $C_{14}H_{20}Cl_2N_3O_3P$: C 44.32, H 5.27, N 11.08, P 8.17, Cl 18.46; found: C 44.22, H 5.18, N 11.16, P 8.24, Cl 18.62.

1-Benzyl-1'-(2-phosphonoethyl)-4,4'-bipyridinium Dichloride (**3d**). ^{1}H-NMR ((D_6)DMSO): 2.40–2.58 (*m*, 2 H); 4.92–5.03 (*m*, 2 H); 5.95 (*s*, 2 H); 7.40–7.60 (*m*, 5 arom. H); 8.71–8.74 (*m*, 4 H); 9.45–9.49 (*m*, 4 H). Anal. calc. for $C_{19}H_{21}Cl_2N_2O_3$: C 53.52; H 4.29, N 6.57, P 7.27, Cl 16.43; found: C 53.82, H 4.20, N 6.48, P 7.24, Cl 16.32.

1-(2,4-Dinitrophenyl)-1'-(2-phosphonoethyl)-4,4'-bipyridinium Dichloride (**3e**). ^{1}H-NMR ((D_6)DMSO): 2.40–2.58 (*m*, 2 H); 4.90–4.95 (*m*, 2 H); 8.43 (*d*, *J* = 8.80, 1 H); 8.42–8.86 (*m*, 6 H); 9.70–9.74 (*d*, *J* = 7.14, 4 H). Anal. calc. for $C_{18}H_{17}Cl_2N_4O_7$: C 43.02, H 3.38, N 11.15, P 6.17, Cl 13.94; found: C 43.10, H 3.26, N 11.26, P 6.10, Cl 13.84.

N,N'-*(Pyridine-2,6-diyl)bis[undecanamide]* (**4a**). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.0, 6 H); 1.25–1.74 (*m*, 36 H); 2.36 (*t*, *J* = 7.6, 4 H); 7.52 (*s*, 2 NH); 7.69 (*t*, *J* = 8.2, 1 H); 7.88 (*d*, *J* = 8.2, 2 H). Anal. calc. for $C_{29}H_{51}N_3O_2$: C 73.53, H 10.85, N 8.87; found: C 73.60, H 10.64, N 8.91.

N,N'-*(Pyridine-2,6-diyl)bis[11-mercaptoundecanamide]* (**5**). ^{1}H-NMR ($CDCl_3$): 1.27–1.37 (*m*, 24 H); 1.54–1.7 (*m*,8 H); 2.33–2.38 (*t*, *J* = 7.5, 4 H); 2.47–2.55 (*dd*, *J* = 7.51, 7.15, 4 H); 7.62 (*s*, 2 H); 7.66–7.72 (*t*, *J* = 8.1, 1 H); 7.88–7.91 (*d*, *J* = 8.1, 2 H). Anal. calc. for $C_{27}H_{47}N_3O_2S_2$: C 63.47, H 9.22, N 8.25, S 12.59; found: C 62.95, H 9.18, N 8.25, S 13.23.

1-Nonyl-1-{{{octadecyl[(1,2,3,6-tetrahydro-2,6-dioxopyrimidin-4-yl)methyl]amino}carbonyl}methyl}-4,4'-bipyridinium Bis(hexafluorophosphate) (**6** · 2 PF_6^-). ^{1}H-NMR ((D_6)acetone): 0.86 (*t*, *J* = 6.7, 6 H); 1.28–1.39 (*m*, 46 H); 3.60 (*t*, *J* = 7.8, 2 H); 4.52 (*s*, 2 H); 5.00 (*t*, *J* = 7.6, 2 H); 5.52 (*s*, 1 H); 6.32 (*s*, 2 H); 7.5 (br. *s*, 1 H); 8.87–8.91 (*dd*, *J* = 5.1, 2.0, 4 H); 9.35 (*d*, *J* = 7.3, 2 H); 9.49 (*d*, *J* = 7.1, 2 H); 9.90 (*s*, 1 H). Anal. calc. for $C_{44}H_{71}F_{12}N_5O_3P_2$: C 52.42, H 7.10, N 6.95; found: C 52.02, H 7.02, N 6.83.

N-*[(1,2,3,6-Tetrahydro-2,6-dioxopyrimidin-4-yl)methyl]*-N-*tridecyldodecanamide* (**7a**). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.0, 6 H); 1.26–1.58 (*m*, 40 H); 2.36 (*t*, *J* = 7.8, 2 H); 4.16 (*s*, 2 H); 5.52 (*s*, 1 H); 8.14 (*s*, 1 H); 9.51 (*s*, 1 H). Anal. calc. for $C_{30}H_{55}N_3O_3$: C 71.25, H 10.95, N 8.39; found: C 71.25, H 10.95, N 8.95.

N-*Butyl-11-mercapto*-N-*[(1,2,3,6-tetrahydro-2,6-dioxopyrimidin-4-yl)methyl]undecanamide* (**7b**). ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, 3 H); 1.23–1.42 (*m*, 14 H); 1.53–1.77 (*m*, 8 H); 2.38–2.41 (*t*, *J* = 7.8, 2 H); 2.49–2.58

(*dd*, J = 7.5, 7.0, 2 H); 3.28–3.35 (*t*, J = 7.8, 2 H); 4.2 (*s*, 2 H); 5.54 (*s*, 1 H); 9.08 (*s*, 1 H); 9.6 (*s*, 1 H). Anal. calc. for $C_{20}H_{35}N_3O_3S$: C 60.45, H 8.80, N 10.57, S 8.06; found: C 59.75, H 8.61, N 9.94, S 7.82.

Eicosylphosphonic Acid (**8**). ^{1}H-NMR ((D_6)DMSO): 0.87 (*t*, J = 6.8, 3 H); 1.1–1.35 (*m*, 34 H); 1.38–1.53 (*m*, 4 H). Anal. calc. for $C_{20}H_{43}O_3P$: C 66.29, H 11.87, P 8.56; found: C 66.13, H 12.22, P 8.53.

1,1'-Dieicosyl-4,4'-bipyridinium Dichloride (**9**). ^{1}H-NMR (CF_3COOD): 0.84 (*t*, J = 7.6, 6 H); 1.27–1.44 (*m*, 68 H); 2.04–2.14 (*m*, 4 H); 4.71–4.76 (*t*, J = 7.33, 4 H); 8.61–8.63 (*dd*, J = 5.86, 4 H, unresolved); 9.03–9.05 (*dd*, J = 5.86, 4 H, unresolved). Anal. calc. for $C_{50}H_{90}Cl_2N_2 \cdot 4\,H_2O$: C 69.76, H 11.39, N 3.25, Cl 8.14; found: C 69.61, H 11.66, N 3.32, Cl 8.35.

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