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Supramolecular photochemistry and photophysics. Adducts of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ with basket-shaped hosts

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$\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ (bpy = 2,2'-bipyridine) can be hosted in basket-shaped hosts containing a diphenylglycoluril unit and aza-polyether handles. Upon adduct formation in CH_2Cl_2 solution at room temperature, the luminescence of both host and guest can no longer be observed, whereas a new, broad, red-shifted emission appears which can be assigned to a charge-transfer transition. Mutual protection of host and guest towards photoreactivity is also observed.

INTRODUCTION

Host-guest systems may exhibit quite interesting photochemical and photophysical properties.¹⁻³ Formation of adducts, in fact, can drastically modify the photochemical and photophysical behavior of the isolated components. Such changes may also give important pieces of information on the intimate structure of host-guest systems.

$\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ (bpy = 2,2'-bipyridine) is a square-planar complex which exhibits most of the properties required to produce stable adducts:⁴ electrical charge and residual interaction ability of the metal ion and of both the bpy and the NH_3 ligands. Furthermore this complex undergoes a clean photochemical reaction in CH_2Cl_2 and exhibits luminescence at low and high temperature in a variety of solvents. Because of these properties $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ has been extensively used as a guest in adducts with aromatic crown ethers and cryptands.⁵⁻⁸

The synthetic receptor **1**⁹ (Fig. 1), contains a cleft based on the concave molecule diphenylglycoluril.

Compound **1** has a well-defined geometry due to the rigidity the fused rings confer on the molecule. Its cleft is of appropriate dimensions to accommodate a flat molecule. Using this building block, a variety of host molecules with interesting binding properties have been constructed.^{9,10} Hosts belonging to this family are the basket-shaped derivatives **2**, **3** and **4**. It has already been shown that **2** and **3** are able to give adducts with alkali metal ions and ammonium ions.¹¹ Compounds **2-4** are

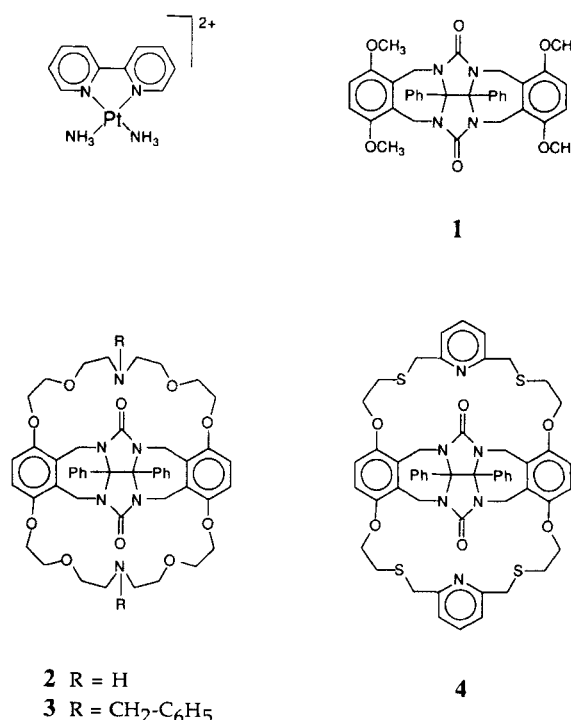


Figure 1 Structure formulas of the investigated compounds.

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also interesting from a photochemical/photophysical point of view since they exhibit an intense fluorescence and some photoreactivity.

Looking at CPK models and considering the properties of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ and **2–4**, we thought that host-guest adducts of photochemical and photophysical interest could be obtained.

EXPERIMENTAL

All solvents and chemicals used in the synthesis were obtained from commercial sources. DMF was distilled under reduced pressure from BaO and degassed prior to use. Dichloromethane was distilled from CaH_2 . Compounds were purified by flash chromatography using silica (Merck Kieselgel 60H). TLC analyses were performed on Merck Kieselgel 60 F254 silica gel plates. All reactions were carried out under an inert atmosphere. ^1H NMR spectra were recorded on a Bruker WH90, ^{13}C NMR spectra on a Bruker WM400. FAB-MS spectra were recorded on a VG 7070E instrument using 3-nitrobenzyl alcohol as a matrix.

The complex $[\text{Pt}(\text{bpy})(\text{NH}_3)_2](\text{PF}_6)_2$ was prepared and purified following literature procedures.¹²

1,3:4,6-Bis[3,3':6,6'-bis(1,4,10,13-tetraoxa-7-azatridecamethylene)-1,2-xylene]tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (**2**) and 1,3:4,6-bis[3,3':6,6'-bis(1,4,10,13-tetraoxa-7-benzyl-7-azatridecamethylene)-1,2-xylene]tetrahydro-3a,6a-diphenylimidazo[4,5-d]imidazole-2,5(1H,3H)-dione (**3**) were prepared and characterized as previously described.¹¹

Compound **4** was synthesized according to the scheme below. 5, 7, 12, 13b, 13c, 14,-Hexahydro-1, 4, 8, 11-tetrakis(2-(thioacetyl)ethoxy)-13b, 13c-diphenyl, 6H, 13H - 5a, 6a, 12a, 13a,-tetraazabenz[5,6]azuleno[2,1,8-ija]benz[f]azulene-6, 13-dione (**5**) was obtained as follows: to 10 mL of dry and degassed DMF was added 603 mg (1.85 mmol) of solid Cs_2CO_3 and 282 mg (3.7 mmol) of thioacetic acid. After the CO_2 evolution had ceased, 500 mg (0.617 mmol) of solid **6**¹³ was added, together with a catalytic amount of NaI. The flask was wrapped in aluminum foil and heated to 60 °C for 20 hrs. Subsequently, the DMF was removed in vacuo and the resulting reddish solid was dissolved in CH_2Cl_2 (150 mL) and washed (2x) with 50 mL of water. The organic

layer was separated, dried over MgSO_4 , filtered and taken to dryness. The resulting yellow solid was further purified by column chromatography (eluent: 0.5 % $\text{MeOH}/\text{CHCl}_3$, v/v) to yield 340 mg (57%) of **5** as a white solid. Rf (TLC, eluent 0.5% MeOH in CHCl_3) = 0.14. ^1H NMR (CDCl_3) δ 7.15 (s, 10 H, ArH), 6.5 (s, 4 H, ArH), 5.5 and 3.7 (2d, 8 H, NCH_2Ar), 3.9 (t, 8H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.2 (t, 8H, $\text{OCH}_2\text{CH}_2\text{S}$), 2.4 (s, 12H, $\text{CH}_3\text{C}(\text{O})$). ^{13}C NMR (CDCl_3) δ 28.77 ($\text{OCH}_2\text{CH}_2\text{S}$), 30.56 ($\text{CH}_3\text{C}(\text{O})\text{S}$), 36.94 (NCH_2Ar), 68.95 ($\text{OCH}_2\text{CH}_2\text{S}$), 85.13 ($\text{NC}(\text{N})\text{Ar}$), 114.39 (XyC), 128.15 (ArC), 134.13 (ArC), 150.47 (ArC), 157.68 ($\text{NC}(\text{O})\text{N}$), 195.54 ($\text{SC}(\text{O})\text{CH}_3$).

Under a dinitrogen atmosphere 100 mg (0.103 mmol) of **5** was dissolved in 2 mL of dichloromethane. To this solution was added 2 mL of a 0.2 M solution of sodium methoxide in methanol. This was stirred for 25 min. at ambient temperature and subsequently a solution of 58 mg (0.219 mmol) of solid 2,6-bis(bromomethyl)pyridine¹⁴ in a mixture of 30 mL of dichloromethane and 30 mL of methanol was added. A white precipitate formed immediately. The mixture was stirred for an additional 3 hrs. The organic layer was washed twice with 25 mL of water. The organic layer was separated, dried (MgSO_4), filtered and concentrated under reduced pressure to yield crude **4**. This product was further purified by column chromatography on silica 60H (eluent 1% MeOH in CHCl_3). Rf(TLC, eluent 2% MeOH in CHCl_3) = 0.24. ^1H NMR (CDCl_3) δ 7.8 (m, 2 H, PyH), 8.3 (m, 1 H, PyH), 7.15 (s, 10 H, ArH), 6.5 (s, 4 H, ArH), 5.5 and 3.7 (2d, 8 H, NCH_2Ar), 4.25 (t, 8H, $\text{OCH}_2\text{CH}_2\text{S}$), 3.9 (m, 8 H, CH_2) 2.9 (m, 8H, $\text{OCH}_2\text{CH}_2\text{S}$). FAB-MS (m-nitrobenzyl alcohol) m/z 1009 ($\text{M} + \text{H}^+$).

The photochemical and photophysical experiments were performed in CH_2Cl_2 distilled over P_2O_5 immediately before use to remove water traces. The equipment and procedures used to measure absorption spectra, luminescence spectra, luminescence lifetimes, and photochemical quantum yields have been described previously.⁵ The quantum yields of the photoreactions of the two components in the adducts were evaluated taking into account the fraction of incident light absorbed by each component.

RESULTS AND DISCUSSION

Properties of the guest

$\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ is not soluble in CH_2Cl_2 , but it can be dissolved in the presence of [18]crown-6 (hereafter indicated by 18C6). Comparison with $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ in acetonitrile solution shows that adduct formation with 18C6 does not modify the spectroscopic and photophysical properties of the complex.^{5,6} The spectrum of $\text{Pt}(\text{bpy})(\text{NH}_3)_2^{2+}$ (Table I) displays a quite intense ab-

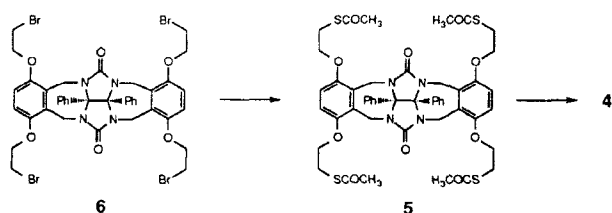


Table 1 Photophysical properties in CH₂Cl₂ of Pt(bpy)(NH₃)₂²⁺, the hosts **2** and **3**, and their adducts

	Absorption		Emission					
	λ_{\max} nm	ϵ_{\max} M ⁻¹ cm ⁻¹	R.T.		77K			
			λ_{\max} nm	τ ns	λ_{\max} nm	τ ns	λ_{\max} nm	τ μ s
Pt-18C6	308 319	12000 18000	455 ^a	100			455 ^a	25
2	295	7600	327	1	325	1	410	1.1 \times 10 ⁶
3	295	7300	327	1	325	1	410	1.1 \times 10 ⁶
Pt- 2	308 321	18800 18400	590	b			460 ^a	18
Pt- 3	308 321	18000 16300	590	1			458 ^a	24

^a) Structured emission; highest-energy feature.

^b) Too low intensity for a good correlation.

sorption in the 290–340 nm region with two peaks located at 308 and 319 nm. At room temperature the complex shows a structured emission (Fig. 2) with a maximum at 488 nm, quantum yield 2.5×10^{-3} , and a lifetime of 100 ns ($\lambda_{\max} = 486$ nm and $\tau = 25$ μ s at 77 K) which has been assigned⁵ to a metal perturbed triplet ligand-centred (³LC) bpy level.

Upon 313 nm irradiation, CH₂Cl₂ solutions of the Pt(bpy)(NH₃)₂²⁺.18C6 adduct undergo a photochemical reaction with $\Phi = 1.4 \times 10^{-2}$ for Pt(bpy)(NH₃)₂²⁺ disappearance.

Properties of the hosts

Compounds **2** and **3** display very similar properties (Table I). They are soluble in CH₂Cl₂ where they exhibit a broad absorption band with a maximum at 295 nm (Table I). Both **2** and **3** exhibit a fluorescence band ($\lambda_{\max} = 327$ nm and $\tau = 1$ ns) in CH₂Cl₂ solution at room temperature (Fig. 2) and fluorescence ($\lambda_{\max} = 325$ nm and $\tau = 1$ ns) and phosphorescence ($\lambda_{\max} = 410$ nm and

$\tau = 1.1$ s) bands in rigid CH₂Cl₂ matrix at 77 K. This behavior is characteristic⁵ of S₁ and T₁ excited states of the *p*-dimethoxybenzene units which are present in the two hosts. Upon 313 nm excitation, in CH₂Cl₂ solution at room temperature both **2** and **3** undergo a photochemical reaction ($\Phi_r = 0.06$ and 0.13, respectively) which causes changes in the absorption spectra and a progressive decrease in the intensity of the luminescence band. Compound **4** displays absorption and emission spectra similar to those of **2** and **3**. Since it does not give adducts with Pt(bpy)(NH₃)₂²⁺, its properties have not been investigated in detail.

Adduct Formation

As mentioned above, [Pt(bpy)(NH₃)₂](PF₆)₂ is not soluble in CH₂Cl₂. A CH₂Cl₂ solution of **4** does not dissolve Pt(bpy)(NH₃)₂²⁺. However, a CH₂Cl₂ solution of **2** or **3** dissolves an equimolar amount of the Pt complex, indicating the formation of a 1:1 adduct. In fact, addition of water to a CH₂Cl₂ solution of the adduct causes the complete separation of the components: **2** or **3** remain in CH₂Cl₂ and Pt(bpy)(NH₃)₂²⁺ goes quantitatively into the aqueous phase as demonstrated by spectral measurements. When a 100 times excess of 18C6 was added to a 1.0×10^{-4} M CH₂Cl₂ solution of the Pt(bpy)(NH₃)₂²⁺•**3** adduct, spectral measurements showed that 40% of the adduct was still associated. This result, confirmed by an experiment performed adding to a 1.0×10^{-4} M solution of Pt(bpy)(NH₃)₂²⁺ containing a 100 times excess 18C6 an equimolar amount of **3**, shows that the basket-shaped host **3** has a much greater affinity for Pt(bpy)(NH₃)₂²⁺ compared with 18C6. Addition of a large excess of NH₄PF₆ to a CH₂Cl₂ solution of **3** does not cause any change in its photophysical properties. Such a solution is not able to dissolve [Pt(bpy)(NH₃)₂](PF₆)₂. This indicates that, when the cavity of the host is occupied by am-

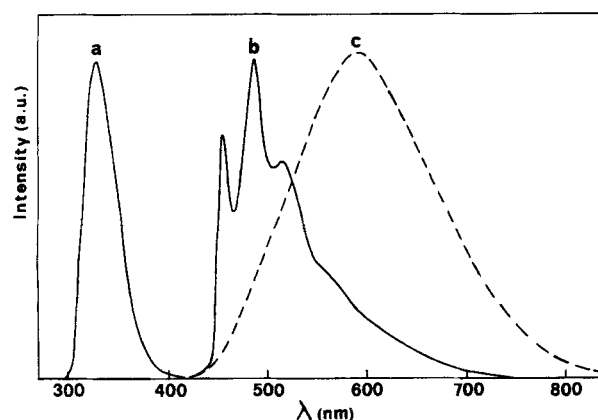


Figure 2 Luminescence spectra (CH₂Cl₂, room temperature), of **3** (a), Pt(bpy)(NH₃)₂²⁺ (b), and of the Pt(bpy)(NH₃)₂²⁺•**3** adduct (c).

monium ions,¹¹ the Pt complex cannot be involved in adducts.

Properties of the adducts

As shown in Fig. 3 and Table I, the absorption spectra of the adducts of Pt(bpy)(NH₃)₂²⁺ with **2** and **3** are different from the sum of the spectra of the two separated components. In particular, there is an increase in absorption in the 260–300 nm region, a decrease in intensity and a small red-shift of the Pt(bpy)(NH₃)₂²⁺ band, and the appearance of a new, broad and weak band in the 340–440 nm region. As far as the luminescence properties are concerned, in CH₂Cl₂ at room temperature adduct formation causes the complete disappearance of the strong fluorescence band at 327 nm characteristic of the dimethoxybenzene units of **2** and **3** and of the ³LC emission ($\lambda_{\text{max}} = 488$ nm) of the platinum complex. A new, broad, red-shifted band appears (Fig. 2) with $\lambda_{\text{max}} = 590$ nm. In the rigid CH₂Cl₂ matrix at 77 K the situation is different since the two adducts show a structured emission identical to that of the Pt(bpy)(NH₃)₂²⁺ component.

From the photochemical view point, the adducts are fairly stable since, in CH₂Cl₂ solution upon 313 nm irradiation, the quantum yields of photodecomposition for the two components in the adduct are at least ten times smaller than those observed for the separated components.

The results obtained indicate that formation of 1:1 adducts of Pt(bpy)(NH₃)₂²⁺ with **2** or **3** takes place with substantial electronic interaction of the chromophoric

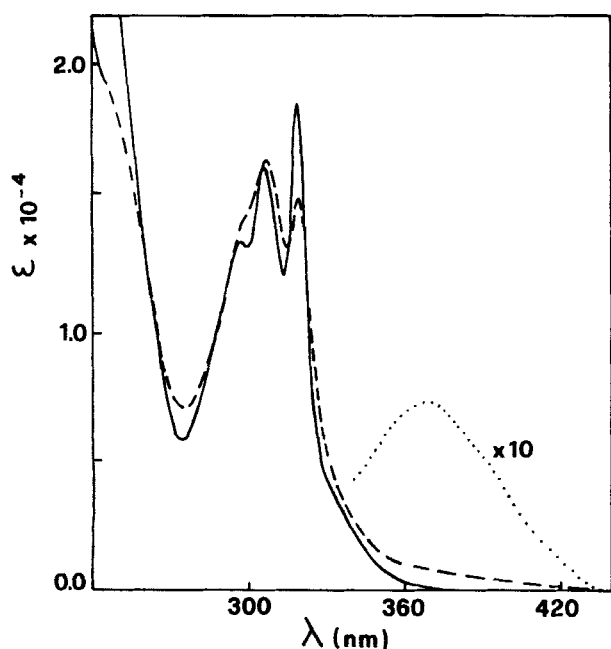


Figure 3 Absorption spectra in CH₂Cl₂ at room temperature: Pt(bpy)(NH₃)₂²⁺+**3** adduct (— —) and sum of the separated components (—). The dotted line shows the difference between the two spectra in the region above 340 nm.

units of the two components. The most important feature is the appearance of low energy charge-transfer excited states that can be assigned, by analogy with the behavior of other similar adducts,^{5–8} to an electronic transition from the electron-rich 1,4-dimethoxybenzene units of the hosts to the empty π^* orbitals of the bpy ligand of the Pt complex. In principle, singlet and triplet charge-transfer levels, ¹CT and ³CT, can be distinguished, the first one responsible for the broad absorption band with maximum around 370 nm, and the second one for the broad emission band with maximum at 590 nm. The large shift between absorption and emission maxima however, is mainly due to excited-state distortion compared to the ground state. As shown in the energy level diagram of Fig. 4, the presence of the CT levels in the adducts favors fast radiationless decay path of the “localized” S₁, T₁, and ³LC levels of the two components. This is the reason why the luminescence of the two components cannot be observed in the adduct. Practically quantitative conversion of the “localized” component levels to the lowest excited state (³CT) of the adduct is shown by the shape of the excitation spectrum which substantially coincides with that of the absorption spectrum. The quenching of the “localized” component levels is also the reason for the almost complete quenching of the photoreactivity of the two components in the adducts.

The different photophysical behavior of the adducts in rigid matrix at 77 K (namely, the disappearance of the ³CT emission observed at room temperature and the appearance of the ³LC luminescence of the Pt complex)

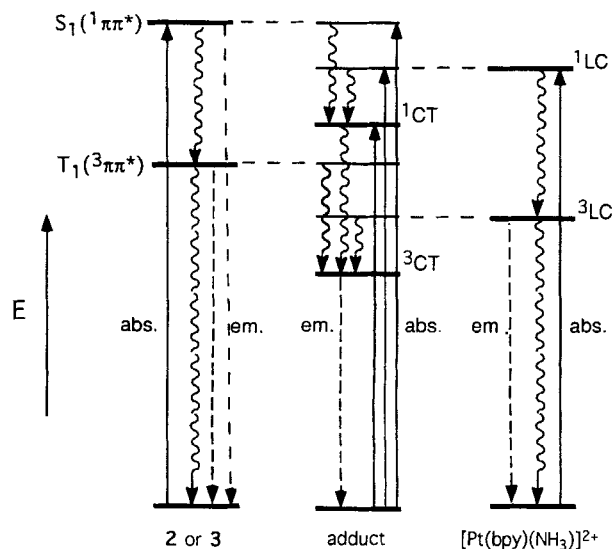


Figure 4 Schematic energy level diagram for the isolated components and their adducts. The reported energy levels correspond to the maxima of the absorption bands for the singlet excited states and to the maxima of the luminescence bands of the triplet excited states (at room temperature for Pt(bpy)(NH₃)₂²⁺ and for the adducts; 77 K for **2** and **3**).

can be explained by the destabilization of the CT levels when the CT transition cannot be accompanied by solvent repolarisation.⁶ Under such circumstances, either the minimum of the luminescent ³CT level lies at higher energy than the ³LC Pt(bpy)(NH₃)₂²⁺ level (which therefore becomes the lowest excited state of the adduct), or a substantial energy barrier, that cannot be overcome at low temperature, separates the ³LC level from the lower lying ³CT level.

In conclusion, adduct formation between Pt(bpy)(NH₃)₂²⁺ and **2** or **3** causes changes in the absorption spectra, luminescent behavior, and photoreactivity. This behavior is very similar to that found for adducts of Pt(bpy)(NH₃)₂²⁺ with various types of aromatic crown ethers and cryptands.⁴⁻⁸ The most likely structure of the adduct is a sandwich-type conformation where the flat Pt complex is inserted in the cleft of the host. This structure allows the stabilization of the adducts *via* both hydrogen bonds and π - π interactions and accounts for the mutual protection of the two components toward their luminescence and photoreactivity. It should be noted that **2**, **3**, and **4** exhibit basket cavities of the same size and shape. Therefore, the lack of adduct formation with **4** must be attributed to worse ability of its handles (compared with those of **2** and **3**) to give hydrogen bonds with the amine ligands of the Pt complex. The donor-acceptor interaction, that is so evident from the absorption, luminescence, and photochemical properties of the adducts of **2** and **3**, is apparently not sufficient to stabilize the adduct. *Vice versa*, hydrogen bond formation is a sufficient condition for adduct formation, as shown by the fact that Pt(bpy)(NH₃)₂²⁺ gives adducts with 18C6.¹⁵

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REFERENCES

- Balzani, V.; Scandola, F.; *Supramolecular Photochemistry*, Horwood, Chichester, **1991**, chapt. 10.
- Schneider, H.-J.; Dürr, H. Eds.; *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Verlag Chemie: Weinheim, **1991**.
- Lehn, J.-M.; *Angew. Chem. Int. Ed. Engl.*, **1988**, *27*, 89.
- Balzani, V.; Ballardini, R.; Gandolfi, M.T.; Prodi, L.; in *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, Schneider, H.-J. and Dürr, H. Eds, Verlag Chemie: Weinheim, **1991**, p.371.
- Ballardini, R.; Gandolfi, M.T.; Prodi, L.; Ciano, M.; Balzani, V.; Kohnke, F.H.; Shahriari-Zavereh, H.; Spencer, N.; Stoddart J.F.; *J. Am. Chem. Soc.*, **1989**, *111*, 7072.
- Gandolfi, M.T.; Zappi, T.; Ballardini, R.; Prodi, L.; Balzani, V.; Stoddart, J.F.; Mathias, J.P.; Spenser N.; *Gazz. Chim. It.*, **1991**, *121*, 521.
- Prodi, L.; Ballardini, R.; Gandolfi, M.T.; Balzani, V.; Desvergne, J.P.; Bouas-Laurent, H.; *J. Phys. Chem.*, **1991**, *95*, 2080.
- Ballardini, R.; Balzani, V.; Credi, A.; Gandolfi, M.T.; Kotzyba-Hibert, F.; Lehn, J.-M.; Prodi, L.; *J. Am. Chem. Soc.*, **1994**, *116*, 5761.
- Smeets, J.W.H.I.; Sijbesma, R.P.; Niele, F.G.M.; Spek, A.L.; Sweets, W.J.J.; Nolte, R.J.M.; *J. Am. Chem. Soc.*, **1987**, *109*, 928.
- (a) Sijbesma, R.P.; Nolte, R.J.M.; *J. Org. Chem.*, **1991**, *56*, 3122; (b) Sijbesma, R.P.; Kentgens, A.M.; Nolte, R.J.M.; *J. Org. Chem.*, **1991**, *56*, 3166.
- Smeets, J.W.H.; van Dalen, L.; Kaats-Richter, V.E.M.; Nolte, R.J.M.; *J. Org. Chem.*, **1990**, *55*, 454.
- (a) Morgan, C.T.; Burstall, F.H.; *J. Chem. Soc.*, **1934**, 965; (b) Colquhoun, H.M.; Doughty, S.M.; Maud, J.M.; Stoddart, J.F.; Williams, D.J.; Wolstenholme, J.B.; *Israel J. Chem.*, **1985**, *25*, 15.
- Sijbesma, R.P.; Nolte, R.J.M.; *Recl. Trav. Chim. Pays-Bas*, **1993**, *112*, 643.
- Offermann, W.; Vögtle, F.; *Synthesis*, **1977**, *3*, 272.
- Colquhoun, H.M.; Stoddart, J.F.; Williams, D.J.; *Angew. Chem. Int. Ed. Engl.*, **1986**, *25*, 487.