

Experimental Section

9aa: 5a (280 mg, 2.0 mmol), triphenylphosphite (49.6 mg, 0.16 mmol), and $[\text{Ir}(\text{cod})\text{Cl}]_2$ (26.9 mg, 0.04 mmol) were stirred in THF (5.0 mL) under an Ar atmosphere. In a separate flask, diethyl malonate (641 mg, 4.0 mmol) was added to a slurry of sodium hydride (96 mg, 4.0 mmol) in THF (5.0 mL). The resulting solution was added to the former by syringe and the combined mixture was stirred at room temperature for 3 h. After **5a** was consumed, diethyl ether and H_2O were added to the mixture, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried (MgSO_4). The solvent was evaporated in vacuo. Purification of the residue by column chromatography (*n*-hexane/*AcOEt* = 98/2) gave **9aa** as a colorless oil (452 mg; yield 94 %).

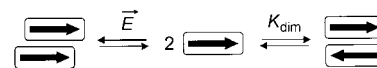
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- [10] When the central metal of an alkyne complex is in a high oxidation state, donation of electrons from an alkyne to the metal should be predominant over back donation from the metal to an alkyne. Oxidative addition of an allylic ester to an iridium(II) species gives an iridium(III) species. The Ir centers in intermediates **18** and **19** would be electron-rich because of the donation of electrons from a coordinated alkyne group.

Dipolar Dye Aggregates: A Problem for Nonlinear Optics, but a Chance for Supramolecular Chemistry**

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The development of nonlinear optical materials requires the optimization of dyes with respect to their molecular electrooptical properties, for example, polarizabilities α , β , and γ ,^[1] as well as their supramolecular organization.^[2] The most investigated $\chi^{(2)}$ nonlinear optical^[3] and photorefractive^[4] polymeric materials require macroscopic noncentrosymmetry, which is achieved through orientation ("poling") of the dipolar dyes by strong external electric fields. Although large dipole moments are considered to be favorable for a high poling efficiency, a large fraction of the materials based on well-designed chromophores with large dipole moments and excellent (hyper)polarizabilities failed to provide the expected electrooptic response.^[5] A possible explanation might be the formation of dye aggregates. According to this concept dipolar dyes are considered to aggregate in an antiparallel fashion as a result of internal electrostatic forces (Scheme 1, right) that counteract the external forces imparted by the electric field during the poling process (Scheme 1, left).^[6, 7]



Scheme 1. Model for the competition between internal organization of dipolar dyes by dipole-dipole interactions (right) and external organization by electric-field-induced dipole orientation leading to a noncentrosymmetric metastable dye arrangement as desired for nonlinear optical applications (left).

Herein we will give proof of this mechanism for merocyanine dyes **1** and **2**, which were recently introduced as the most suitable candidates for photorefractive applications on the basis of their molecular properties.^[8] However, their incorporation into polymers was critical and led us to use less-dipolar dyes based on aminothiophene and indoline electron-donor groups, for example, dyes **3** and **4**.^[9]

The first evidence for strong homoaggregation of dyes **1** and **2**, respectively, came from concentration-dependent UV/Vis spectra, which showed distinct hypsochromically shifted aggregate bands ("H-aggregates") already in dilute solution for solvents with low polarity (Figure 1). The well-defined isosbestic points over the whole accessible concentration range suggest the formation of dimer aggregates, which could be further confirmed by vapor-pressure osmometry (VPO).^[10] From the large hypsochromic shifts of about 70 nm and 117 nm (**2**) in the absorption bands we deduce the (**1a-h**)

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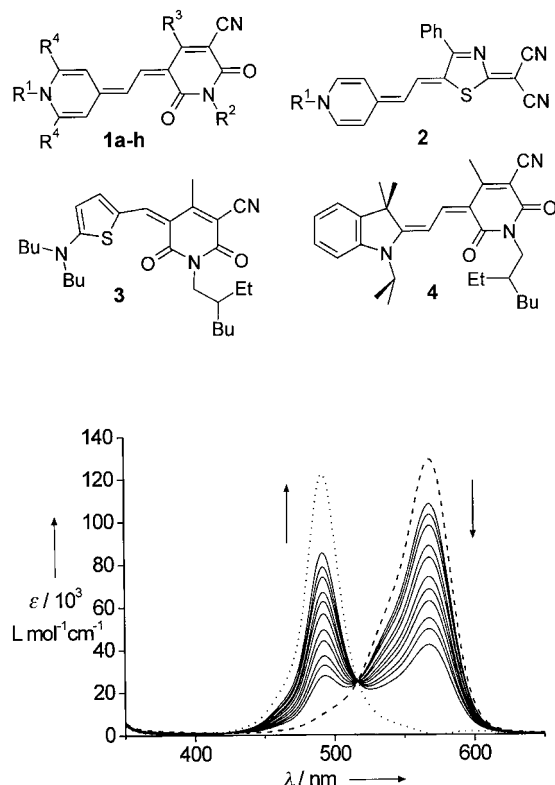


Figure 1. Concentration-dependent UV/Vis spectra of dye **1a** in dioxane. The arrows indicate increasing concentrations from 1.5×10^{-6} to $3 \times 10^{-5} \text{ mol L}^{-1}$. The apparent extinction coefficients ϵ were calculated according to the Beer–Lambert law, and the spectra of the monomer (---, $\lambda_{\text{max}} = 569 \text{ nm}$) and the dimer (···, $\lambda_{\text{max}} = 492 \text{ nm}$) were obtained from the data at two different concentrations and the calculated binding constant. Almost identical spectral changes are observed for dyes **1b–h**.

existence of closely packed dyes with almost parallel transition dipole moments, which is in accordance with exciton coupling theory.^[11]

Interestingly these dimer aggregates proved to be energetically and structurally very stable supramolecular motifs. The Gibbs free dimerization energies of dyes **1** and **2** are comparable to the highest interaction energies reported for supramolecular systems in low-polarity environments and the values in more-polar solvents, such as chloroform, still exceed those of the often used triple-hydrogen bonds (Table 1).^[12] This interaction energy may be reduced significantly if several sterically demanding substituents are attached to the central part of dyes **1** (R^3 , R^4).^[13] On the other hand, even the sterically most demanding *tert*-butyl substituent did not reduce the dimerization constant if it was attached at the outer pyridine nitrogen atom (R^1).

The structural characterization of the dimer aggregates was accomplished by dipole moment and two-dimensional NMR measurements.^[13] Figure 2 shows the results of dipole moment determinations for dye **1h** in comparison to the weakly aggregating dye **3**. From the slopes of the linear regression analyses the dipole moments are calculated^[14] as 12 D for **3** but only about 5 D for **1h**. The value for **3** is in reasonable agreement with the value of 14 D obtained from electro-optical absorption measurements (EOAM) in highly dilute solutions,^[9] whereas the value for **1h** is contrary to the EOAM

Table 1. Dimerization constants K_{dim} and Gibbs free dimerization energies ΔG^0 for dyes **1a–h** and **2–4** from UV/Vis dilution studies at 20 °C in various solvents.^[a,b]

Dye	R^1	R^2	R^3	R^4	Solvent	$K_{\text{dim}} [\text{L mol}^{-1}]$	$-\Delta G^0 [\text{kJ mol}^{-1}]$
1a	Hex	Hex	Me	H	dioxane	105 000	28.2
1b	Bu	Hex	Me	H	dioxane	121 000	28.5
1c	sBu	Hex	Me	H	dioxane	52 000	26.5
1d	tBu	Hex	Me	H	dioxane	116 000	28.4
1e	sBu	iPr	Pr	H	dioxane	9700	22.4
1f	Dodec	sPent	Pr	iPr	dioxane	900	16.6
1g	Dodec	Dodec	Me	H	CCl_4	2×10^7	41
					dioxane	132 000	28.7
					CHCl_3	520 ^[c]	15.2
					THF	65	10.2
1h	Ethex	Ethex	Me	H	dioxane	47 000	26.2
2	Hex				dioxane	8×10^6	39
					CHCl_3	36 000	25.5
					dioxane	50	9.5
4					dioxane	< 5	< 4 ^[d]

[a] Average from nonlinear regression analyses at four to six different wavelengths of the monomer and the dimer absorption band. The standard deviations are about $\pm 0.2 \text{ kJ mol}^{-1}$ for ΔG^0 . Each dye was studied at a minimum of eight different concentrations in cells of appropriate pathlengths (0.01 to 50 mm). [b] sPent = 2-pentyl; Ethex = 2-ethylhexyl; Dodec = 1-dodecyl. [c] The same value was obtained in a NMR dilution experiment in CDCl_3 as determined by the change in ^1H chemical shifts. [d] No aggregation was observed up to a concentration of $2 \times 10^{-2} \text{ mol L}^{-1}$.

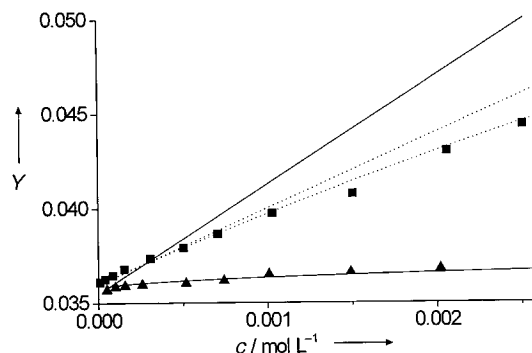


Figure 2. Dipole moment measurements of dyes **1h** (▲) and **3** (■) in dioxane with $Y = (\epsilon_r - 1)/(\epsilon_r + 2) - (n^2 - 1)/(n^2 + 2)$. The lines show the calculations according to Equation (1) and for the nonaggregating dyes with $\mu = 17 \text{ D}$ (**1h**, —) and for $\mu = 14 \text{ D}$ (**3**, ···), respectively.

value of 17 D.^[8b] Clearly, only an antiparallel orientation of the dipolar dyes in the dimer aggregate can account for this observation and indeed a calculation according to Equation (1) reproduced the experimental data for both dyes **1h** and **3** fairly well if dipole moments of zero were assumed for the dimers:

$$\mu^2 = \frac{1}{c_T} (c_M \mu_M^2 + c_D \mu_D^2) \quad (1)$$

where μ denotes the dipole moment, c the concentration of the monomeric (M) and the dimeric (D) species as calculated from the binding data given in Table 1, and c_T is the total concentration of dye. A major conclusion can be drawn from Figure 2: highly dipolar dyes **1h** do not orient in the given external electric field because of the much larger internal field within the dipolar aggregate (Scheme 1).

The strong coupling of the optical transitions, the antiparallel orientation of the dipole moments, and the insensitivity of the binding constant towards the size of the substituent at the pyridine nitrogen atom suggest a slightly slipped aggregate structure (Figure 3).^[11] This structural model was further

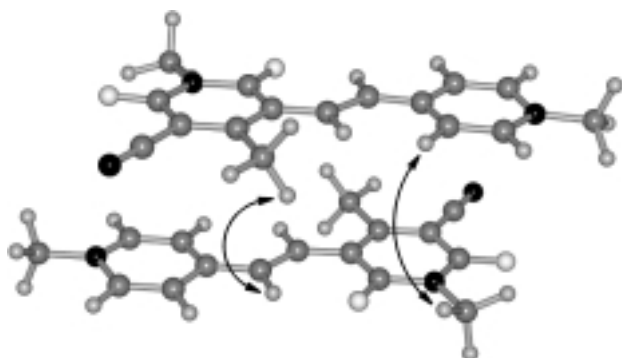


Figure 3. Proposed structure of **1a–h** dimer aggregates based on NMR, UV/Vis, and dipole moment data. The arrows indicate spatial proximities as evidenced by ROESY NMR cross peaks in $[D_8]$ dioxane at 20°C. The drawing was generated from AM1 geometry optimized molecules **1** with all its alkyl substituents replaced by methyl groups for simplicity.^[15]

supported by two-dimensional NMR experiments for **1h** in $[D_8]$ dioxane, which revealed distinct ROESY cross peaks between two pairs of protons that are at remote positions of the individual dye molecules but in spatial proximity in the dimer aggregate (~ 3 Å according to molecular modeling studies^[15]).

Finally, it seemed interesting to take a closer look at the effects of the solvent on the dimerization equilibrium and so provide evidence for the intermolecular forces involved. Therefore, dimerization energies ΔG^0 were determined from concentration-dependent UV/Vis spectra of dye **1g** in a number of solvents and linear free energy relationships were explored between ΔG^0 values and empirical solvent scales ($E_T - 30$, Z , π^*) as well as the Kirkwood–Onsager polarity function ($\epsilon_r - 1$)/(2 $\epsilon_r + 1$), which is based on the macroscopic permittivity ϵ_r of the solvent.^[16] By far the best fit was obtained using the Kirkwood–Onsager function (Figure 4). Here, the only solvent with a significant deviation was dioxane,^[17] whereas all the other solvents could be fitted by linear regression analysis with an impressive correlation

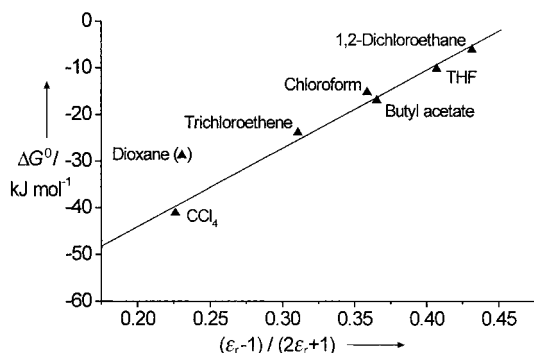


Figure 4. Dependence of the Gibbs dimerization energy for **1g** on the Kirkwood–Onsager polarity function of the solvent.

coefficient of 0.993, a mean standard deviation of only 1.7 kJ mol⁻¹ for the respective ΔG^0 values, and a point of intersection with the y axis at $\Delta G^0 = -78$ kJ mol⁻¹, which corresponds to the gas phase dimerization energy ($\epsilon_r = 1$). Since the Kirkwood–Onsager function considers only electrostatic contributions to describe the solvent polarity, these results provide strong evidence that the main intermolecular forces involved in the dimerization process are indeed electrostatic dipole–dipole interactions as suggested by Scheme 1. Accordingly, the dimerization mechanism and the solvent dependence clearly distinguish these dipolar dye aggregates from well-known aggregates of ionic dyes in water where aggregation is mainly driven by dispersion interactions and the hydrophobic effect.^[18]

In conclusion, the dimer aggregates studied in this work support an often assumed mechanism used to explain unexpected low nonlinear optical susceptibilities in polymeric materials based on electric-field-poled dipolar dyes. The high magnitude of the dimerization constants observed for dyes **1** and **2** are a very promising starting point for a number of projects directed towards functional supramolecular structures such as tweezers and macrocyclic hosts for encapsulation of dipolar molecules, as well as supramolecular polymers.

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Chiral 1,1'-Diphosphetanylferrocenes: New Ligands for Asymmetric Catalytic Hydrogenation of Itaconate Derivatives**

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The attainment of both high catalytic efficiency and high enantioselectivity remains a formidable challenge in asymmetric catalysis.^[1] Bidentate ligands composed of *trans*-2,5-disubstituted phospholane groups have been shown to be useful in asymmetric catalytic hydrogenation reactions.^[2] Despite high enantioselectivities, practical application of this technology frequently requires enhancement of catalyst activity and productivity. To augment the turnover frequencies of catalysts bearing bis(phospholane) ligands, we introduced more flexible backbones (for example, 1,3-propandiyl and 1,1'-ferrocene bridges).^[3] Whereas catalytic rates were greatly improved in these systems, enantioselectivities were found to plummet. We now have found that the combination of efficiency and selectivity may be realized through use of phosphetanes. Here we outline the synthesis of new 1,1'-diphosphetanylferrocene ligands (**1**; FerroTANE)^[4] and demonstrate the superiority of these ligands over known systems in the highly efficient and enantioselective Rh-catalyzed hydrogenation of itaconate derivatives.

The first optically active phosphetanes previously were described in seminal reports by Marinetti and Ricard.^[5] More recently, we^[6] and the group of Marinetti and Genêt^[7] have independently prepared and examined enantiomerically pure 2,4-disubstituted phosphetanes for use as ligands in asymmetric catalysis. The chiral 2,4-disubstituted phosphetane moiety may be constructed from readily available enantiomerically pure 1,3-diols. The requisite 1,3-diols were prepared conveniently through asymmetric hydrogenation of 1,3-diketones using well-documented procedures involving biaryldi-phosphane–Ru catalysts.^[8] Subsequently, the diols were converted to 1,3-diol cyclic sulfates **3** through treatment with thionyl chloride followed by Ru-catalyzed oxidation with sodium periodate.^[6,7] As shown in Scheme 1, the reaction between the cyclic sulfates **3** and the known diphosphanylferrocene **2**^[3b] provided facile access to the desired ligands **1a–e**, which were isolated as yellow to orange crystalline solids in moderate to good overall yields. A wide range of different 2,4-disubstituted FerroTANE ligands may be obtained through this procedure. The facility with which ligand **1e** (R = *t*Bu) was formed is particularly surprising considering

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