Hybrid Materials Doped with Covalently Bound Perylene Dyes through the Sol−Gel Process

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We synthesized solubilized alkoxysilane-modified perylene derivatives which were covalently attached to an inorganic host matrix, prepared via the sol−gel process. It was shown that the covalent attachment of the alkoxysilane-modified perylenes led to more homogeneous sols and higher concentrations of the dyes in the sol than the physical admixing of corresponding derivatives. Furthermore, we found that modifying the inorganic network with organic groups caused better solubility characteristics for the perylene derivatives. Attachment of the alkoxysilane-modified perylene derivatives was improved using a more reactive network precursor such as zirconium *n*-propoxide. Monoliths were prepared by using special temperature programs developed for each sol. Photostability tests of these monoliths showed that chemical attachment of the chromophores led to a significant improvement in the photostability in comparison to their physically admixed analogues.

Introduction

The sol−gel process[1−3] is a well-known technique for forming inorganic−organic glasslike materials. Using this method, a network-former and a network-modifier can be combined to develop materials with attractive properties, in particular to mechanical, thermal, and chemical stability. In addition alkoxysilane monomers, the alkoxides,[4] alcoholates, or halogenides of titanium, zirconium, aluminum, or boron are used as network-forming reagents.[5,6] The metalates are first transformed into the corresponding hydroxides by controlled hydrolysis and condensation reactions, catalyzed by acid or base, which result in the inorganic oligomers or polymers upon removal of water.[7]

The substitution of the alkoxide group at the silane by an alkyl or aryl allows modification of the inorganic network with organic groups.[1] In this way composite materials with high transparency can be prepared. Another possibility to establish unprecedented material properties is the incorporation of fillers such as titanium dioxide or aerosils or the doping of the composites with molecules such as fullerenes[8] or dyes.[9−12] Sol−gel glasses doped with organic chromophores have numerous applications such as dye-lasers,[13] nonlinear optical materials,[14] biosensors, or luminescence solar collectors.[15] Dyes are normally physically incorporated into the hybrid matrix. With suitable functionalization of the dye molecules they can also be covalently attached to the silica network.[16] In the case of the azochromophore disperse red 1, this method leads to higher concentrations and better orientation of the dye molecules in an electric field.[17]

Dyes derived from perylene,[18−20] e.g., perylene-3,4-dicarboximides **1** and perylene-3,4:9,10-tetracarboxdiimides **2**, as shown in Chart 1, have particularly attractive optical properties. While they are highly fluorescent, their advantage over the azochromophores or the rhodamine dyes is high photostability, which renders them interesting for industrial applications.[21]

In this paper we present novel perylene derivatives which are covalently bound to different sol−gel matrixes; we further compare the different methods of incorporation of the perylenes into the sol−gel matrix (physical admixing and chemical attachment) with respect to the maximum potential concentration of the dyes and the photostability of the monoliths prepared from the sols.

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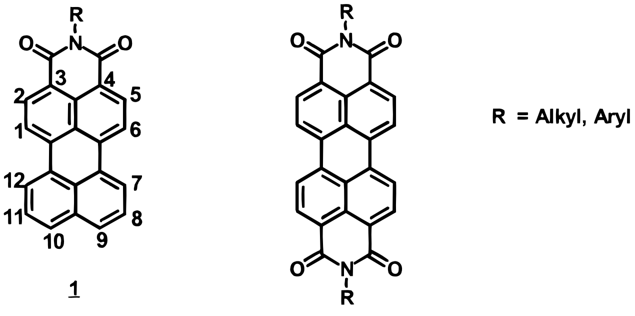
Chart 1. Perylene Derivatives: Perylene-3,4-dicarboximides 1 and Perylene-3,4:9,10-tetracarboxdiimides 2



1

2

Experimental Section

Instrumental Methods. ^{1}H and ^{13}C NMR Spectroscopy: Bruker AC 300 MHz and Bruker AMX 500. ^{29}Si NMR spectroscopy: Bruker AMX 500. Mass spectrometry, field desorption (FD): Finnigan MAT 312. Infrared spectroscopy: Nicolet FT-IR 320. UV−vis absorption spectroscopy: Perkin-Elmer Lambda 9. Melting points (uncorrected): Büchi melting point apparatus. Elemental analyses were performed at the Department of Chemistry and Pharmacy of the University of Mainz. Photostability tests were carried out at BASF AG: xenotest 450 with a lightening power of 810 W/m^2 (<800 nm) for a maximal 1000 h. Valuation was made by the pseudologarithmic woolscale[22] with marks from 1 to 8 (best mark, no bleaching after 1000 h of lightening).

Solvents used were commercial p.a. quality, THF was purified and dried according to standard procedures,[23] and ethanol and methanol were kept over molecular sieves. The silanes used were purchased from ABCR. Perylene derivatives used as starting materials were provided by BASF AG or synthesized as described in the referenced literature.

Monomer Synthesis. *N*-(3-Triethoxysilyl)propylperylene-3,4-dicarboxmonoimide (3). A 644 mg (2 mmol) sample of perylenedicarboxylic monoanhydride (**4**), purified by extraction, was added to a 250 mL round-bottomed Schlenk flask containing a magnetic stirring bar, followed by 100 mL of dry ethanol. The flask was evacuated and flushed with argon several times. The mixture was stirred for 1/2 hour under an argon atmosphere, after which 1.77 g (8 mmol) of freshly distilled (3-aminopropyl)triethoxysilane (APTES) (**5**) was added dropwise. The reaction mixture was refluxed under argon for 24 h. After the mixture was cooled to room temperature, the precipitate was collected by suction filtration. The obtained red powder was washed with cold ethanol. After the powder was dried in a vacuum over silica gel the desired product was isolated in 82% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.34 (d, ^{3}J(H,H) = 8.23 Hz, 2H, Ar−H); 8.19 (d, ^{3}J(H,H) = 7.69 Hz, 2H, Ar−H); 8.12 (d, ^{3}J(H,H) = 8.24 Hz, 2H, Ar−H); 7.79 (d, ^{3}J(H,H) = 8.24 Hz, 2H, Ar−H); 7.50 (t, ^{3}J(H,H) = 7.69 Hz, 2H, $H_{8,11}$); 4.13 (t, ^{3}J(H,H) = 8.23 Hz, 2H, $N-CH_2$); 3.82 (q, ^{3}J(H,H) = 7.31 Hz, 6H, OCH_2); 1.82 (m, 2H, $N-CH_2-\mathit{CH_2}$), 1.21 (t, ^{3}J(H,H) = 7.13 Hz, 9H, $OCH_2\mathit{CH_3}$); 0.78−0.75 (m, 2H, $Si-CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 163.71 (C═O); 136.75; 134.13; 131.15; 130.72; 129.47; 128.96; 127.63; 126.88; 126.42; 123.43; 120.73; 119.90; 58.42 (OCH_2); 42.87 ($N-CH_2$); 29.13 ($N-CH_2-\mathit{CH_2}$); 18.31 ($OCH_2\mathit{CH_3}$); 8.10 ($Si-CH_2$). FD-MS: *m*/*z* (u e_0^{-1}) found 525.6 (100, M^+), calcd 525.67. IR (KBr): 1693 ($\nu_{C=O}$); 1638 ($\nu_{C=O}$); 1104 (ν_{C-O}); 1079 (ν_{Si-O-C}) cm^{-1}; UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 264 (28 579); 319 (4934); 331 (4339); 485 (32 421); 507 (30 177). Anal. Calcd for $C_{31}H_{31}NO_5Si$: C, 70.83; H, 5.94; N, 2.66. Found: C, 57.84; H, 6.34; N, 4.61 (the differences between the found and calculated values of the elemental analysis will be discussed in the Results and Discussion section).

***N*-(3-Trimethoxysilyl)propylperylene-3,4-dicarboxmonoimide ("Dimer") (6).** A 644 mg (2 mmol) sample of perylenedicarboxylic monoanhydride (**4**), 100 mL of dry methanol, and 1.432 g (0.008 mol) of (3-aminopropyl)trimethoxysilane (APTMS) (**7**) were refluxed under an argon atmosphere for 24 h. After suction filtration the obtained powder was washed with cold methanol. The product was isolated in 86% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.33 (d, ^{3}J(H,H) = 8.25 Hz, 2H, Ar−H); 8.20 (d, ^{3}J(H,H) = 7.72 Hz, 2H, Ar−H); 8.11 (d, ^{3}J(H,H) = 8.23 Hz, 2H, Ar−H); 7.78 (d, ^{3}J(H,H) = 8.24 Hz, 2H, Ar−H); 7.50 (t, ^{3}J(H,H) = 7.74 Hz, 2H, $H_{8,11}$); 4.12 (t, ^{3}J(H,H) = 8.20 Hz, 2H, $N-CH_2$); 3.48 (s, 6H, OCH_3); 1.81 (m, 2H, $N-CH_2-\mathit{CH_2}$); 0.76 (m, 2H, $Si-CH_2$). ^{29}Si NMR solid CP-MAS: δ (ppm) = −48 (T^1). FD-MS: *m*/*z* (u e_0^{-1}) found 920.3 (100, M^+), calcd 920.26. IR (KBr): 1689 ($\nu_{C=O}$); 1643 ($\nu_{C=O}$); 1108 (ν_{C-O}); 1075 (ν_{Si-O-C}); 1038 w ($\nu_{Si-O-Si}$) cm^{-1}; UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 267 (8092); 319 (5971); 379 (1607); 489 (27 975); 514 (25 856). Anal. Calcd for $C_{54}H_{44}N_2O_9Si_2$: C, 70.41; H, 4.81; N, 3.04. Found: C, 69.90; H, 4.76; N, 3.07.

***N*,*N*′-Bis(3-triethoxysilylpropyl)-perylene-3,4:9,10-tetracarboxdiimide (8).** A 0.785 g (2 mmol) sample of 3,4:9,10-perylenetetracarboxylic bisanhydride (**9**) (BASF) (purified by repeatedly being dissolved in potassium hydroxide solution and reprecipitated with HCl) was added to a 250 mL Schlenk flask, followed by 70 mL of dry ethanol. The flask was repeatedly evacuated and flushed with argon. After the mixture was stirred for 1/2 h under an argon atmosphere, it was heated in an oil bath to 110 °C. A 3.542 g (16 mmol) sample of (3-aminopropyl)triethoxysilane (APTES) (**5**) was added dropwise through a septum. The reaction mixture was stirred for 6 h under reflux and under an inert atmosphere. After the mixture was cooled to room temperature, the precipitate was collected by suction filtration and washed thoroughly with cold ethanol. The dark red product was obtained in 82% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.60 (d, ^{3}J(H,H) = 7.93 Hz, 4H, Ar−H); 8.53 (d, ^{3}J(H,H) = 7.93 Hz, 4H, Ar−H); 4.14 (t, ^{3}J(H,H) = 7.33 Hz, 4H, $N-CH_2$); 3.78 (q, ^{3}J(H,H) = 6.71 Hz, 12H, OCH_2); 1.84 (m, 4H, $N-CH_2-\mathit{CH_2}$), 1.18 (t, ^{3}J(H,H) = 7.32 Hz, 18H, $OCH_2\mathit{CH_3}$); 0.70 (m, 4H, $Si-CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 164.44 (C═O); 135.70; 132.59; 130.33; 127.42; 124.35; 124.25; 59.57 (OCH_2); 42.75 ($N-CH_2$); 22.70 ($N-CH_2-\mathit{CH_2}$); 19.55 ($OCH_2\mathit{CH_3}$); 9.29 ($Si-CH_2$). FD-MS: *m*/*z* (u e_0^{-1}) found 798.0 (100, M^+), calcd 798.30. IR (KBr): 1693 ($\nu_{C=O}$), 1655 ($\nu_{C=O}$) cm^{-1}. UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 260 (47 507); 458 (14 267); 489 (36 089); 525 (57 007). Anal. Calcd for $C_{42}H_{50}N_2O_{10}Si_2$: C, 63.13; H, 6.31; N, 3.51. Found: C, 58.81; H, 6.18; N, 3.78.

***N*,*N*′-Bis(3-triethoxysilylpropyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetra-carboxdiimide (10).** The mixture of 0.1 g (0.131 mmol) of 1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic bisanhydride (**11**)[24] and 0.1745 g (0.789 mmol) of (3-aminopropyl)triethoxysilane (**5**) in 30 mL of dry ethanol was reacted under reflux and an inert atmosphere for 4.5 h. After suction filtration and washing of the obtained powder with cold ethanol, the product was isolated in 72% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C) δ (ppm) = 8.26 (s, 4H, H2); 7.27 (m, 4H, H4′); 7.13 (m, ^{3}J(H,H) = 7.69 Hz, 4H, H3′); 6.96 (d, ^{3}J(H,H) = 7.14 Hz, 4H, H2′); 4.12 (t, ^{3}J(H,H) = 7.68 Hz, 4H, $N-CH_2$); 3.82 (q, ^{3}J(H,H) = 7.13 Hz, 12H, OCH_2); 1.84−1.78 (m, 4H, $N-CH_2-\mathit{CH_2}$), 1.21 (t, ^{3}J(H,H) = 7.14 Hz, 18H, $OCH_2\mathit{CH_3}$); 0.71 (m, 4H, $Si-CH_2$). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 163.18 (C═O); 155.80 (C1); 155.38 (C1′); 132.82; 129.94; 124.53; 122.73; 120.51; 120.06; 119.94; 119.63; 58.38 (OCH_2); 43.04 ($N-CH_2$); 21.51 ($N-CH_2-\mathit{CH_2}$); 18.26 ($OCH_2\mathit{CH_3}$); 8.01 ($Si-CH_2$). ^{29}Si NMR (99.38 MHz, $CCCl_3$, 30 °C): δ (ppm) = −45.8 (T^0_0). FD-MS: *m*/*z* (u e_0^{-1}) found 1166.9 (100, M^+), calcd 1166.41. IR (KBr):

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1699 ($\nu_{C=O}$), 1660 ($\nu_{C=O}$) cm^{-1}. UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 286 (44 261); 444 (14 218); 539 (26 015); 576 (33 797). Anal. Calcd for $C_{66}H_{66}N_2O_{14}Si_2$: C, 67.90; H, 5.70; N, 2.40. Found: C, 68.36; H, 5.83; N, 2.76.

***N*,*N*′-Bis(3-triethoxysilylpropyl)-1,6,7,12-tetrakis(4′-hexyloxyphenoxy)perylene-3,4:9,10-tetracarboxdiimide (12).** The mixture of 58 mg (0.05 mmol) of 1,6,7,12-tetrakis(4′-hexyloxyphenoxy))perylene-3,4:9,10-tetracarboxylic bisanhydride (**13**)^{24} and 88.5 mg (0.4 mmol) of (3-aminopropyl)triethoxysilane (**5**) in 20 mL of dry ethanol was reacted under reflux and an inert atmosphere for 4.0 h. After suction filtration and washing of the obtained powder with cold ethanol, the product was isolated in 68% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ (ppm) = 8.07 (s, 4H, H2); 6.88 (d, ^3J(H,H) = 8.79 Hz, 8H, H3′); 6.79 (d, ^3J(H,H) = 8.74 Hz, 8H, H2′); 4.06 (t, ^3J(H,H) = 7.68 Hz, 4H, N−CH$_2$); 3.91 (t, ^3J(H,H) = 6.59 Hz, 8H, Ar−OCH$_2$); 3.75 (q, ^3J(H,H) = 7.14 Hz, 12H, OCH$_2$); 1.76 (m, 12H, N−CH$_2$−*CH$_2$*, Ar−OCH$_2$−*CH$_2$*); 1.45 (m, 8H, CH$_2$); 1.34 (m, 16 H, (CH$_2$)$_2$); 1.16 (t, ^3J(H,H) = 6.59 Hz, 18H, OCH$_2$*CH$_3$*); 0.90 (m, 12H, CH$_3$); 0.66 (m, 4H, Si−CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ (ppm) = 163.34 (C═O); 156.62 (C4′); 156.21 (C1); 148.44 (C1′);132.80; 122.42; 121.39; 119.85; 119.10; 118.97; 115.96; 77.0 (Ar−O−CH$_2$); 58.37 (OCH$_2$); 43.03 (N−CH$_2$); 31.60 (β-CH$_2$) 29.27 (γ-CH$_2$); 25.74 (CH$_2$); 22.62 (CH$_2$); 21.51 (N−CH$_2$−*CH$_2$*); 18.26 (OCH$_2$*CH$_3$*); 14.04 (CH$_3$); 7.99 (Si−CH$_2$). FD-MS: m/z (u e$_0$$^{-1}$) found 1567.7 (100, M$^+$), calcd 1566.76. IR (KBr): 1698 ($\nu_{C=O}$), 1661 ($\nu_{C=O}$) cm^{-1}. UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 282 (52 148); 462 (6749); 550 (12 311); 591 (17 666).

***N*,*N*′-Bis(3-triethoxysilylpropyl)-1,7-diphenoxyperylene-3,4,9:10-tetracarboxdiimide (14).** The mixture of 100 mg (0.173 mmol) of 1,7-diphenoxyperylene-3,4:9,10-tetracarboxylic bisanhydride (**15**)^{24} and 153.6 mg (0.694 mmol) of (3-aminopropyl)triethoxysilane (**5**) in 20 mL of dry ethanol was reacted under reflux and an inert atmosphere for 3.5 h. After suction filtration and washing of the obtained powder with cold ethanol, the product was isolated in 55% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ (ppm) = 9.58 (d, ^3J = 8.24 Hz, 2H, H6,12); 8.65 (d, ^3J(H,H) = 8.53 Hz, 2H, H5,11); 8.31 (s, 2 H, H2,8); 7.46 (m, 4 H, Ar−H); 7.29 (m, 2H, H4′); 7.16 (m, ^3J = 7.93 Hz, 4 H, Ar−H); 4.09 (m, 4H, N−CH$_2$); 3.80 (q, ^3J(H,H) = 6.72, 12H, OCH$_2$); 1.84 (m, 4H, N−CH$_2$−*CH$_2$*); 1.20 (t, ^3J(H,H) = 7.30 Hz, 18H, OCH$_2$*CH$_3$*); 0.73 (m, 4H, Si−CH$_2$). ^{13}C NMR (75 MHz, CDCl$_3$, 25 °C): δ (ppm) = 163.12 (C═O); 162.71 (C═O); 155.06; 154.84; 130.44; 130.14; 128.71; 127.67; 125.00; 124.89; 124.20; 124.03; 123.03; 122.22; 119.33; 119.21; 58.40 (OCH$_2$); 43.06 (N−CH$_2$); 21.51 (N−CH$_2$−*CH$_2$*); 18.26 (OCH$_2$*CH$_3$*); 7.99 (Si−CH$_2$). FD-MS: m/z (u e$_0$$^{-1}$) found 983.2 (100, M$^+$), calcd 983.23. IR (KBr): 1699 ($\nu_{C=O}$), 1662 ($\nu_{C=O}$) cm^{-1}; UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 265 (44 391), 393 (9337), 406 (9216), 505 (42 504), 532 (48 605). Anal. Calcd for $C_{54}H_{58}N_2O_{12}Si_2$: C, 65.97; H, 5.95; N, 2.85. Found: C, 64.50; H, 5.72; N, 3.50.

***N*,*N*′-Bis(3-triethoxysilylpropyl)-1,7-bis(4′-*tert*-butylphenoxy)perylene-3,4:9,10-tetracarboxdiimide (16).** The mixture of 50 mg (0.0726 mmol) of 1,7-bis(4′-hexyloxyphenoxy)-perylene-3,4:9,10-tetracarboxylic bisanhydride (**17**)^{24} and 128 mg (0,578 mmol) of (3-aminopropyl)triethoxysilane (**5**) in 20 mL of dry ethanol was reacted under reflux and an inert atmosphere for 3.5 h. After suction filtration and washing of the obtained powder with cold ethanol, the product was isolated in 52% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, CDCl$_3$, 25 °C): δ (ppm) = 9.57 (d, ^3J(H,H) = 8.39 Hz, 2H, H6,12); 8.55 (d, ^3J(H,H) = 8.39 Hz, 2H, H5,11); 8.30 (s, 2 H, H2,8); 7.41−7.38 (m, 4H, H3′); 7.05−7.02 (m, 4H, H2′); 4.08 (t, 4H, N−CH$_2$); 3.74 (q, ^3J(H,H) = 7.25 Hz, 12H, OCH$_2$); 1.79 (m, 4H, N−CH$_2$−*CH$_2$*); 1.36 (s, 18H, (CH$_3$)$_3$); 1.13 (t, ^3J(H,H) = 6.87 Hz, 18H, OCH$_2$*CH$_3$*); 0.69 (m, 4H, Si−CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ (ppm) = 163.31 (C═O); 162.96 (C═O); 155.40 152.76; 148.12; 130.14; 129.42; 128.91; 128.80; 127.38; 124.34; 124.09; 124.01; 123.91; 122.33; 118.95; 58.35 (OCH$_2$); 43.01 (N−CH$_2$); 34.49 (*C*(CH$_3$)$_3$); 31.40 (C(*CH$_3$*)$_3$); 21.53 (N−CH$_2$−*CH$_2$*); 18.18 (OCH$_2$*CH$_3$*); 8.11 (Si−CH$_2$). FD-MS: m/z (u e$_0$$^{-1}$) found 1094.0 (100, M$^+$), calcd 1094.47. IR (KBr): 1698 ($\nu_{C=O}$), 1659 ($\nu_{C=O}$) cm^{-1}. UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 295 (5310), 433 (8246); 539 (27 944), 574 (36 210). Anal. Calcd for $C_{62}H_{74}N_2O_{12}Si_2$: C, 67.98; H, 6.81; N, 2.56. Found: C, 67.58; H, 6.16; N, 2.75.

***N*,*N*′-Bis(3-triethoxysilylpropyl)-1,6,7,12-tetrakis[4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy]perylene-3,4:9,10-tetracarboxdiimide (18).** A 200 mg (0.165 mmol) sample of 1,6,7,12-tetrakis(4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxy)perylene-3,4:9,10-tetracarboxylic bisanhydride (**19**)^{24} was added to a 50 mL Schlenk flask, followed by 20 mL of dry ethanol. The flask was repeatedly evacuated and flushed with argon. After the reaction mixture was stirred for 0.5 h under an argon atmosphere, it was heated in an oil bath to 100 °C. A 73.2 mg (0.32 mmol) sample of (3-aminopropyl)triethoxysilane (**5**) was added through a septum. The reaction mixture was stirred for 2 h under an inert atmosphere, while the color changed from orange to dark red. The solvent was immediately evaporated under a vacuum and the remaining powder rapidly washed with ice-cold ethanol. The dark red product was isolated in 85% yield. Mp > 300 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ (ppm) = 8.10 (s, 4H, H2); 7.25 (d, ^3J(H,H) = 8.54 Hz, 8H, H3′); 6.84 (d, ^3J(H,H) = 8.54 Hz, 8H, H2′); 4.06 (t, ^3J(H,H) = 7.33 Hz, 4H, N−CH$_2$); 3.76 (q, ^3J(H,H) = 6.71 Hz, 12H, OCH$_2$); 1.77 (m, 4H, N−CH$_2$−*CH$_2$*); 1.71 (s, 8H, CH$_2$); 1.34 (s, 24H, (CH$_3$)$_2$); 1.16 (t, ^3J(H,H) = 7.32 Hz, 18H, OCH$_2$*CH$_3$*); 0.76 (s, 36H, (CH$_3$)$_3$); 0.66 (m,^3J(H,H) = 8.55 Hz, 4H, Si−CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ (ppm) = 163.27 (C═O); 156.17 (C1); 152.70 (C1′); 146.62 (C4′);132.71; 127.67; 122.54; 120.11; 119.56; 119.27; 119.02; 58.36 (OCH$_2$); 57.11 (*C*(CH$_3$)$_2$) 42.98 (N−CH$_2$); 38.35 (*C*(CH$_3$)$_3$); 32.42 (C(*CH$_3$*)$_2$); 31.82 (C(*CH$_3$*)$_3$); 31.52 (CH$_2$); 21.49 (N−CH$_2$−*CH$_2$*); 18.25 (OCH$_2$*CH$_3$*); 7.99 (Si−CH$_2$). ^{29}Si NMR (99.38 MHz, CDCl$_3$, 30 °C): δ (ppm) = −45.82 (T^0$_0$). FD-MS: m/z (u e$_0$$^{-1}$) found 1615.6 (100, M$^+$), calcd 1614.91; IR (KBr): 1700 ($\nu_{C=O}$), 1664 ($\nu_{C=O}$) cm^{-1}; UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 268 (43 739); 287 (55 546); 449 (17 815); 548 (32 596); 585 (42 347). Anal. Calcd for $C_{98}H_{130}N_2O_{14}Si_2$: C, 72.83; H, 8.11; N, 1.73. Found: C, 69.00; H, 8.56; N, 2.70.

***N*-(3-Triethoxysilylpropyl)carbamide Acid 6-(3′-Hexylperylene-9′(10′)-yl)hexyl Ester (20).** A 0.8 g (1.83 mmol) sample of 3-hexyl-9(10)-(6′-hydroxyhexyl)perylene (21)^{25} was added to a 100 mL Schlenk flask, followed by 60 mL of dry tetrahydrofuran. The flask was repeatedly evacuated and flushed with argon. A 0.906 g (3.664 mmol) sample of (3-isocyanatopropyl)triethoxysilane (IPTES) (**22**) was added under an argon atmosphere. The reaction mixture was heated in an oil bath to 60 °C and stirred for 16 h. The solvent was evaporated, and the remaining powder was washed with ice-cold methanol. It was again dissolved in THF and slowly reprecipitated by addition of methanol/pentane (1:1). The orange product was obtained in 38% yield. For absolute purification a separation by GPC with THF as solvent was possible. However, with this method, the yield was drastically reduced. Mp 100.93 °C. ^{1}H NMR (500 MHz, CDCl$_3$, 25 °C): δ (ppm) = 8.23−8.19 (m, ^3J(H,H) = 7.68 Hz, 2H, H6,12); 8.12−8.10 (m, ^3J(H,H) = 7.13 Hz, 2H, H1,7); 7.88 (m, ^3J(H,H) = 8.24 Hz, 2H, H5,11); 7.53 (m, ^3J(H,H) = 7.68 Hz, 2H, H4,10); 7.34 (m, 2H, H2,8); 4.87 (s, 1H, N−H); 4.07 (t, 2H, CO−O−CH$_2$); 3.82 (q, ^3J(H,H) = 7.14 and 6.59 Hz, 6H, OCH$_2$); 3.17 (m, 2H, N−CH$_2$); 3.03 (t, ^3J = 8.24 Hz, 4H, Ar−CH$_2$); 1.81−1.75 (m, 4H, CH$_2$); 1.65 (m, 6H, CH$_2$); 1.49 (m, 4H, CH$_2$); 1.37 (m, 4H, CH$_2$); 1.23 (t, ^3J(H,H) = 7.14 Hz, 9H, OCH$_2$*CH$_3$*); 0.93 (t, ^3J = 7.13 Hz, 3H, CH$_3$); 0.64 (m, ^3J = 7.68 Hz, 2H, Si−CH$_2$). ^{13}C NMR (125 MHz, CDCl$_3$, 25 °C): δ (ppm) = 156.69 (C═O); 138.17; 132.99; 132.04; 129.73; 128.84; 127.34; 126.90; 126.78; 126.18; 125.62; 123.63; 123.09; 120.61; 119.97; 119.55; 64.70 (*CH$_2$*−O−CO); 58.43 (O*CH$_2$*CH$_3$); 43.09 (N−CH$_2$); 33.24 (Ar−CH$_2$); 31.76; 30.44; 29.91; 29.51; 28.78; 28.01; 25.83 (N−CH$_2$−*CH$_2$*); 22.65; 18.69 (OCH$_2$*CH$_3$*); 13.61 (CH$_3$); 7.65 (Si−CH$_2$). ^{29}Si NMR (99.38 MHz, CDCl$_3$, 30 °C): δ (ppm) = −45.54 (T^0$_0$). FD-MS: m/z (u e$_0$$^{-1}$) found 683.4 (100, M$^+$), calcd 683.40; IR (KBr): 1688 ($\nu_{C=O}$) cm^{-1}. UV (CHCl$_3$): λ_{max} (nm) (ϵ (M^{-1}

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(25) Schlichting, P.; Rohr, U.; Müllen, K. *Liebigs Ann./Recl.* **1997**, 395−407.

cm^{-1})) = 257 (31 307); 401 (11 118); 424 (23 196); 452 (28 808). Anal. Calcd for $C_{42}H_{57}NO_5Si$: C, 73.75; H, 8.40; N, 2.05. Found: C, 73.78; H, 8.55; N, 2.16.

3,9(10)-Perylenedicarboxylic Acid Di[5′-yl-*N*-(3-triethoxysilylpropyl)]pentyl Ester (23). A 54 mg (0.1 mmol) sample of 3,9(10)-perylenedicarboxylic acid di[5′-hydroxy]-pentyl ester (**24**),[26] dissolved in 20 mL of dry pyridine, was added to a 50 mL Schlenk flask. After repeated evacuation and flushing of the flask with argon, 148 mg (0.6 mmol) of (3-isocyanatopropyl)triethoxysilane (**22**) was added. The mixture was stirred at 80 °C for 4 h, after which the solvent was evaporated. The residue was stirred in methylene chloride under an inert atmosphere for 1 h. The undissolved particles (oligomers of the product) were separated by filtration. The solvent was evaporated and the orange product obtained in 34% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.89 (m, 2H, Ar−H); 8.80 (m, 2H, Ar−H); 8.27−8.20 (m, 2H, Ar−H); 8.16−8.14 (m, 2H, Ar−H); 7.60 (m, 2H, Ar−H); 4.64 (s, 2H, N−H); 4.36 (m, 4H, Ar−CO−O−CH_2); 4.00 (m, 2H, N−CO−O−CH_2); 3.75 (q, ^3J(H,H) = 7.26, 6.86 Hz, 12H, OCH_2); 3.11 (m, 4H, N−CH_2); 1.98 (m, 4H, CH_2); 1.78 (m, 8H, CH_2); 1.55−1.43 (m, 8H, CH_2); 1.20 (t, 18H, OCH_2CH_3); 0.76 (m, 4H, Si−CH_2). FD-MS: m/z (u e_0^{-1}) found 1034.3 (100, M$^+$), calcd 1034.49. IR (KBr): 1709 ($\nu_{C=O}$), 1637 ($\nu_{C=O}$) cm^{-1}. UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 348 (2026); 439 (24 230); 465 (28 947). Anal. Calcd for $C_{52}H_{74}N_2O_{14}Si_2$: C, 62.64; H, 7.59; N, 2.71. Found: C, 54.86; H, 6.02; N, 6.78.

Bis-*N*-(3-triethoxysilylpropyl)carbamide Acid 6-[Perylene-3,9(10)-diyl]hexyl Ester (25). A 125 mg (0.276 mmol) sample of bis-3,9(10)-(6′-hydroxyhexyl)perylene (**26**)[25] was added to a 50 mL Schlenk flask, followed by 25 mL of dry THF. After repeated evacuation and flushing of the flask with argon, 417 mg (1.69 mmol) of (3-isocyanatopropyl)triethoxysilane (**22**) was added. The mixture was stirred at 60 °C for 1 day under argon. Another 209 mg (0.845 mmol) sample of (3-isocyanatopropyl)-triethoxysilane (**22**) was added, and the mixture was again stirred for 1 day at 60 °C. After the mixture was cooled to room temperature, the solvent was evaporated. The obtained solid was dissolved in 60 mL of dry methylene chloride and stirred for 1 h. The undissolved particles were removed by filtration. The solvent was evaporated and the powder washed with cold methanol. The yellow product was obtained in 68% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.20−8.15 (m, 2H, H6,12); 8.11−8.06 (m, 2H, H1,7); 7.85−7.81 (m, 2H, H5,11); 7.51−7.45 (m, 2H, H4,10); 7.32−7.29 (m, 2H, H2,8); 4.85 (s, 2H, N−H); 4.05−4.01 (m, 4H, CO−O−CH_2); 3.80 (q, ^3J(H,H) = 7.18 and 6.88 Hz, 12H, OCH_2); 3.15−3.13 (m, 4H, N−CH_2); 2.99 (t, ^3J = 7.97 Hz, 4H, Ar−CH_2); 1.75−1.72 (m, 4H, CH_2); 1.59−1.56 (m, 8H, CH_2); 1.43−1.40 (m, 8H, CH_2); 1.19 (t, ^3J(H,H) = 7.14 Hz, 18H, OCH_2CH_3); 0.63−0.57 (m, 4H, Si−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ (ppm) = 156.40 (C═O); 137.82; 132.58; 131.64; 129.31; 128.46; 126.40; 126.34; 125.83; 119.60; 119.15; 64.64 (CH_2−O−CO); 58.04 (OCH_2CH_3); 43.07 (N−CH_2); 32.85 (Ar−CH_2); 30.05; 29.05; 28.67; 25.44 (N−CH_2−CH_2); 22.94; 17.85 (OCH_2CH_3); 7.25 (Si−CH_2). FD-MS: m/z (u e_0^{-1}) found 946.7 (100, M$^+$), calcd 946.52; IR (KBr): 1690 ($\nu_{C=O}$), 1635 ($\nu_{C=O}$) cm^{-1}. UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 259 (36 357); 404 (12 911); 427 (26 938); 456 (33 455). Anal. Calcd for $C_{52}H_{78}N_2O_{10}Si_2$: C, 65.93; H, 8.30; N, 2.96. Found: C, 62.09; H, 7.72; N, 4.69.

Bis-*N*-(3-Triethoxysilylpropyl)carbamide Acid 5-[Perylene-3,9(10)-diyl]pentyl Ester (27). The reaction was performed as described for perylene derivative **25**. Reaction of 42.46 mg (0.1 mmol) of bis-3,9(10)-(6′-hydroxypentyl)perylene (**28**)[25] and 148.42 mg (0.6 mmol) (second addition, 74.21 mg (0.3 mmol)) of (3-isocyanatopropyl)triethoxysilane (**22**) in 15 mL of dry THF afforded the yellow product in 72% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.15−8.10 (m, 2H, H6,12); 8.06−8.01 (m, 2H, H1,7); 7.80−7.75 (m, 2H, H5,11); 7.47−7.44 (m, 2H, H4,10); 7.27−7.24 (m, 2H, H2,8); 4.89 (s, 2H, N−H); 4.01 (m, 4H, CO−O−CH_2); 3.81−3.70 (q, ^3J(H,H) = 6.87 u. 7.25 Hz, 12H, OCH_2); 3.11 (m, 4H, N−CH_2); 2.95 (t, ^3J = 7.63 Hz, 4H, Ar−CH_2); 1.75−1.67 (m, 4H, CH_2); 1.62−1.52 (m, 8H, CH_2, N−CH_2−CH_2); 1.49−1.44 (m, 4H, CH_2); 1.15 (t, ^3J(H,H) = 7.25 Hz, 18H, OCH_2CH_3); 0.58−0.53 (m, 4H, Si−CH_2). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ ppm) = 156.78 (C═O); 138.44; 138.04; 132.96; 132.05; 129.76; 128.87; 126.84; 126.35; 126.29; 123.64; 123.27; 120.04; 119.61; 64.72 (CH_2−O−CO); 58.45 (OCH_2CH_3); 43.38 (N−CH_2); 33.24 (Ar−CH_2); 30.23; 29.04; 26.13 (N−CH_2−CH_2); 23.34; 18.43 (OCH_2CH_3); 7.66 (Si−CH_2). FD-MS: m/z (u e_0^{-1}) found 918.2 (100, M$^+$), calcd 918.48. IR (KBr): 3347 (N−H), 1694 ($\nu_{C=O}$), 1643 ($\nu_{C=O}$) cm^{-1}. UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 259 (32 724); 404 (11 621); 427 (24 246); 456 (30 112). Anal. Calcd for $C_{50}H_{74}N_2O_{10}Si_2$: C, 65.33; H, 8.11; N, 3.05. Found: C, 62.63; H, 7.55; N, 5.56.

6,6′-Di[3,9(10)-perylenediyl]hexanoic Acid Di(3-triethoxysilyl)propylamide (29). (a) A 0.240 g (0.5 mmol) sample of 3,9(10)-bis(5′-carboxypentyl)perylene (**30**)[25] was added to a 100 mL Schlenk flask, followed by 40 mL of dry toluene and 10 mL of dry dimethylformamide. The flask was repeatedly evacuated and flushed with argon. The mixture was heated to 80 °C under argon and stirred until all starting material was dissolved, after which 0.494 g (2 mmol) of (3-isocyanatopropyl)triethoxysilane (**22**) was added through a septum. The reaction mixture was stirred under reflux for 16 h. The solvent was evaporated and the residue thoroughly washed with cold ethanol several times. The powder was dissolved in dry THF and reprecipitated by slow addition of pentane. The product was collected by vacuum filtration in 54% yield. (b) A 0.100 g (0.208 mmol) sample of 3,9(10)-bis-(5′-carboxypentyl)perylene (**30**) was added to a 100 mL Schlenk flask, followed by 50 mL of dry THF. The flask was repeatedly evacuated and flushed with argon. A 0.264 g (2.08 mmol) sample of oxalyl chloride was slowly added at room temperature. The mixture was stirred under reflux for 6 h. The solvent and excess oxalyl chloride were evaporated. A 50 mL portion of dry THF and 2 mL of dry pyridine were added to the resulting acyl chloride-modified perylene **31**, followed by 0.046 g (0.208 mmol) of freshly distilled (3-aminopropyl)-triethoxysilane (**5**). The mixture was stirred at 30 °C for 2 h, after which the solvents were immediately evaporated and the remaining powder was washed with cold ethanol, dissolved in dry THF, and reprecipitated with hexane. The product was obtained in 50% yield. Mp > 300 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ (ppm) = 8.18−8.12 (m, 2H, H6,12); 8.09−8.03 (m, 2H, H1,7); 7.80 (m, 2H, H5,11); 7.46 (m, 2H, H4,10); 7.29−7.26 (m, 2H, H2,8); 4.89 (s, 2H, N−H); 4.07 (q, ^3J(H,H) = 7.95, 7.14 Hz, 12H, OCH_2); 3.21−3.18 (m, 4H, N−CH_2); 2.97 (t, ^3J = 7.71 Hz, 4H, Ar−CH_2); 2.14 (t, 4H, CH_2−CO−NH); 1.74−1.71 (m, 4H, CH_2); 1.63−1.52 (m, 8H, CH_2); 1.47−1.44 (m, 4H, CH_2); 1.21 (t, 18H, OCH_2CH_3); 0.82 (m, 4H, Si−CH_2). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ (ppm) = 172.88 (C═O); 158.33; 156.71; 156.29 138.07; 132.93; 132.01; 129.95; 126.79; 126.24; 119.96; 119.55; 119.52; 58.44 (OCH_2CH_3); 33.11 (Ar−CH_2); 31.54; 30.82; 29.38; 25.64; 25.11; 23.56; 22.89; 18.23 (OCH_2CH_3); 7.60 (Si−CH_2). FD-MS: m/z (u e_0^{-1}) found 887.3 (100, M$^+$), calcd 886.50. IR (KBr): 1701 ($\nu_{C=O}$), 1644 ($\nu_{C=O}$) cm^{-1}. UV ($CHCl_3$): λ_{max} (nm) (ϵ (M^{-1} cm^{-1})) = 259 (34 504); 402 (12 253); 425 (25 565); 453 (31 750). Anal. Calcd for $C_{50}H_{74}N_2O_8Si_2$: C, 67.68; H, 8.41; N, 3.16. Found: C, 66.97; H, 8.35; N, 3.25.

Formulation of Sols with Chemically Attached Perylene Derivatives. For each type of sol one example is given. The concentration of the dye is calculated with respect to the ideal cured matrix (which implies complete hydrolysis and condensation of all alkoxy groups). The water for the hydrolysis reactions was added in the form of 0.1 N HCl, whereby the molar ratio between water and the alkoxy groups of the used silanes was 0.5.

Methyltriethoxysilane (MTEOS)−Tetraethoxysilane (TEOS) Sol. In a 50 mL Schlenk flask, 23 mg (1.5 wt % referring to the ideal cured matrix) of one of the alkoxysilane-modified perylene derivatives (e.g., **18**) was dispersed in 10 mL of dry THF. A 0.2 mL sample of 0.1 N HCl was added, and the mixture was stirred at 60 °C for 2 h under an inert atmosphere. In another 50 mL Schlenk flask, 2.6 g (0.0125

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[26] Müller, G. Ph.D. Thesis, University of Mainz, 1997.

Chart 2. Perylene Derivatives for Physical Admixture to the Sol−Gel Matrix

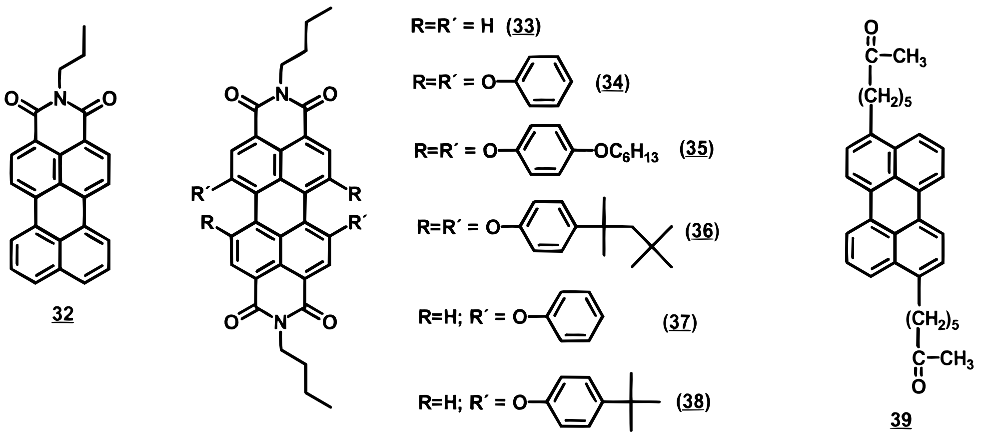


Table 1. Perylene Derivatives for Physical Admixture and Their Corresponding Derivatives for Chemical Attachment

perylene derivative for physical admixture	32	33	34	35	36	37	38	39
corresponding perylene derivative for covalent attachment	**3** and **6**	**8**	**10**	**12**	**18**	**14**	**16**	**20**, **23**, **25**, **27**, and **29**

Table 2. Temperature Programs for the Different Sols

	MTEOS−TEOS	MTEOS−TEOS−GPTS	TEOS−GPTS−DPSD	MPTS−Zr−GPTS
45 °C	5 h	5 h	5 h	5 h
65 °C	4 h	4 h	5 h	4 h
80 °C	3 h	3 h	1 h	4 h
100 °C	5 h	5 h	7 h	6 h

mol) of TEOS and 2.23 g (0.0125 mol) of MTEOS were stirred with 0.2 mL of 0.1 N HCl at room temperature under inert conditions until the initially two-phase mixture became a one-phase mixture, the so-called “clearing-point”.

At this point the alkoxysilane-modified perylene derivative which was prehydrolyzed and 10 mL of dry ethanol were added to the silanes. The reaction mixture was stirred at 60 °C for 1 day under argon, and then an additional 0.4 mL of 0.1 N HCl was added. The reaction time varied depending on the type of application, e.g., films and monoliths. For films the sol was stirred for 1 day further, for monoliths 2 days.

MTEOS−TEOS−(Glycidoxypropyl)triethoxysilane (GPTS) Sol. In a 50 mL Schlenk flask, 0.272 g (0.001 15 mol) of GPTS, 27 mg (3 wt % referring to the ideal cured matrix) of an alkoxysilane-modified perylene derivative (e.g., **18**), 5 mL of dry THF, 5 mL of dry ethanol, and 0.05 mL of 0.1 N HCl were stirred under reflux for 2 h. In another flask, 0.907 g (0.005 09 mol) of MTEOS and 1.3 g (0.006 24 mol) of TEOS were stirred with 0.15 mL of 0.1 N HCl at room temperature until the clearing point was reached. Then both mixtures were poured together and stirred at 60 °C for 1 day under argon. After further addition of 0.2 mL of 0.1 N HCl, the reaction mixture was again stirred for 1 day (2 days) in the case of films (monoliths).

GPTS−TEOS−Diphenylsilanediol (DPSD) Sol. In a 50 mL Schlenk flask, 31.9 mg (1.5 wt %) of an alkoxysilane derivative of perylene (e.g., **18**), 1.182 g (0.005 mol) of GPTS, 1.082 g (0.005 mol) of DPSD, 5 mL of dry THF, and 5 mL of dry ethanol were stirred at 60 °C until a homogeneous dispersion was reached. A 1.04 g (0.005 mol) sample of TEOS, catalyzed by 0.32 mL of 0.1 N HCl, was stirred at room temperature until the clearing point was reached. Both mixtures were poured together and stirred at 60 °C for 36 h under argon. For monolith preparation the reaction time was at least 2.5 days.

GPTS−(Methacryloxypropyl)trimethoxysilane (MPTS)−Zirconium Sol. In a 50 mL Schlenk flask, 135 mg (3.5 wt %) of an alkoxysilane-modified perylene derivative (e.g., **18**) was dissolved in 12 mL of dry THF. A 0.14 mL sample of 0.1 N HCl was added. The solution was stirred under reflux and inert conditions for 2 h. A 1.18 g (0.005 mol) sample of GPTS was added, and the mixture was stirred for 1 h. During this time 2.48 g (0.01 mol) of MPTS was prehydrolyzed with 0.27 mL of 0.1 N HCl in another flask until the clearing point (∼2.5 min), after which 4.679 g (0.01 mol zirconium) of zirconium *n*-propoxide solution (70% in propanol) was slowly added under stirring. The MPTS−zirconium *n*-propoxide solution was added to the prehydrolyzed perylene derivative, followed by 12 mL of dry ethanol. After the mixture was stirred at 60 °C for 2 h under an inert atmosphere, 0.36 mL of 0.1 N HCl was added. After a further 16 h (34 h) at 60 °C, the sol could be used for film (monolith) preparation.

The hydrolysis and condensation rates of the alkoxysilanes, forming the network, and the alkoxysilane-modified perylene derivatives were controlled using ^{29}Si NMR spectroscopy.

Formulation of Sols with Physically Admixed Perylene Derivatives. In comparison to the former section, in this section we will describe the incorporation of perylene derivatives which are not able to react with alkoxysilanes during the sol−gel process.

The same sol synthesis described in the previous section was used with the exception of prehydrolysis of these perylene derivatives, which was inapplicable. The perylene derivatives were only dissolved in THF and added to the silane precursors, forming the network.

Each perylene derivative which was used for physical admixing was classed with a corresponding alkoxysilane-modified derivative as shown in Chart 2 and Table 1.

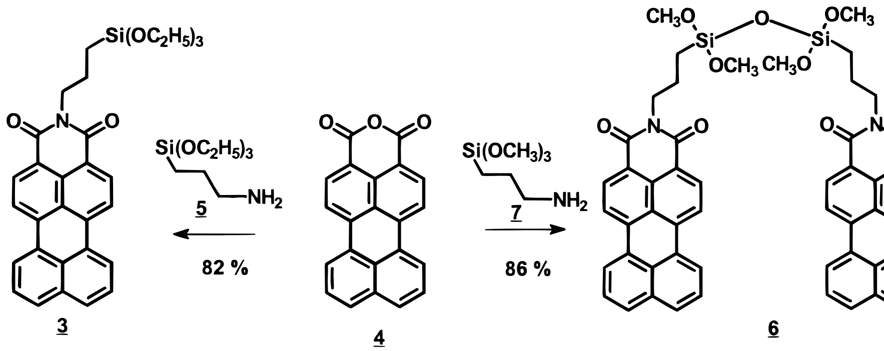
Monolith Preparation. The solvent of the sol was evaporated at 15 mbar and 55 °C bath temperature until a highly viscous (honeylike) sol was obtained. The measured viscosities (viscobalance at 25 °C, 70% solution in ethanol) of the MTEOS−TEOS−(GPTS) sols were between 70 and 80 mPa s, of the DPSD sol between 60 and 70 mPa s, and of the MPTS−Zr−GPTS sol between 82 and 92 mPa s. It was necessary to pour the sol immediately into a Teflon vessel to avoid gelation in the flask. The bulk materials were cured using the temperature programs, which all have a heating rate of 1 K/min, given in Table 2.

The GPTS−TEOS−DPSD sol builds elastic, rubberlike monoliths, whereas the monoliths of the other sols are brittle.

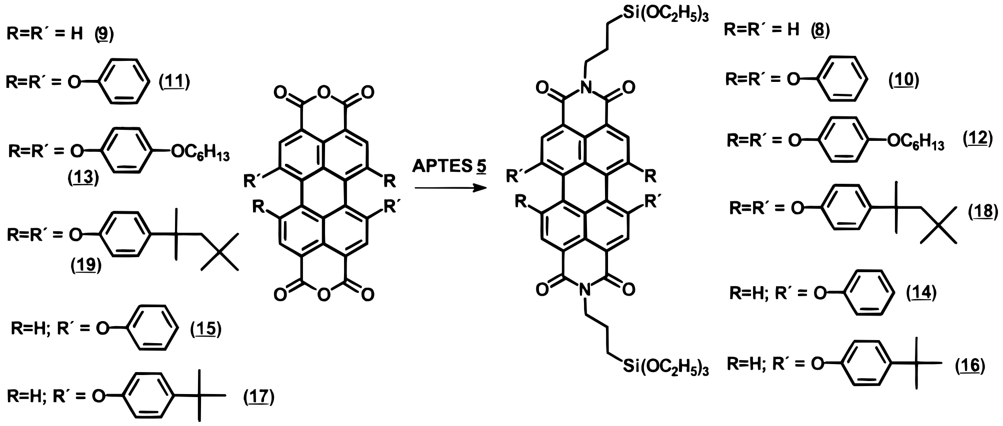
3. Results and Discussion

Synthesis of Alkoxysilane-Modified Peryleneimides. For a chemical attachment of the perylenes to

Scheme 1. Condensation of Perylenedicarboxylic Anhydrides with (Aminoalkyl)trialkoxysilanes



Scheme 2. Synthesized Alkoxysilane-Modified Perylenetetracarboxdiimides



the inorganic network, a suitable functionalization is necessary. We synthesized alkoxysilane-modified perylene derivatives, which were able to react with the alkoxysilanes, forming the network during the sol−gel process, by hydrolysis and condensation reactions.

Starting with commercially available perylenedicarboxylic monoanhydride (**4**), condensation reactions with (ω-aminoalkyl)trialkoxysilanes led to the corresponding silane derivatives as shown in Scheme 1.

It is known[27] that methoxy groups are more reactive toward nucleophilic substitution reactions than ethoxy groups. This fact was also confirmed by the condensation reaction mentioned above. ^{29}Si NMR spectroscopy and mass spectrometry showed that in the case of (3-aminopropyl)trimethoxysilane (APTMS) (**7**) only the dimer of *N*-(3-trimethoxysilyl)propylperylene-3,4-dicarboximide (**6**) was obtained, whereas using (3-aminopropyl)triethoxysilane (APTES) (**5**), *N*-(3-triethoxysilyl)-propylperylene-3,4-dicarboximide (**3**) was isolated as the monomer. Solubility studies have shown that dimers such as **6** or oligomers have a lower solubility in comparison to the corresponding monomers. Thus, it is difficult to incorporate them homogeneously in the sol−gel matrix and also impossible to reach a high concentration of the dyes in the host matrix. In the case of **3** we were able to incorporate 0.5 wt % in the sol−gel matrix, whereas less than 0.5 wt % **6** was incorporated. Therefore, in further experiments only ethoxysilanes were used.

To improve the solubility of peryleneimide in the matrix, resulting in a higher concentration of the dye, we synthesized a peryleneimide with an alkoxysilane chain on both sides of the perylene core via a condensation reaction of 3,4:9,10-perylenetetracarboxylic dianhydride (**9**) and APTES (**5**). The resulting *N*,*N*′-bis(3-triethoxysilylpropyl)perylene-3,4:9,10-tetracarboxdiimide (**8**) however showed no significant improvement, and it was also only slightly soluble in THF (<1 mg/mL), a solvent used in the sol−gel process.

From the experiments above it was evident that the core of the perylene plays an important role in the solubility behavior of the alkoxysilane-modified perylenes. Therefore, our next aim was to modify the structure of the perylene and to increase its solubility by introducing phenoxy groups in the *bay* positions.[24] Scheme 2 shows the synthesized derivatives of alkoxysilane-modified perylene-3,4:9,10-tetracarboxdiimides, whereby the same reaction technique was used as for the synthesis of **8**.

Among all perylenetetracarboxdiimides compound **18** has the best solubility in THF (>60 mg/mL).

Synthesis of Alkoxysilane-Modified 3,9(10)-Substituted Perylenes. Within the scope of color tuning we were not satisfied with the incorporation of only red peryleneimides, but were looking for suitable perylenes with other absorption behavior.

In addition to the well-known peryleneimides, 3,9- and 3,10-substituted, the so-called *peri*-substituted perylenes are also described in the literature.[25,28−30] We were interested in the 3,9- and 3,10-dialkylperylenes which are ω-functionalized at one or both alkyl chain ends.[25] These *peri*-substituted perylenes absorb in the

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(29) Pongartz, A. *Monatsh. Chem.* **1927**, *48*, 585−591.

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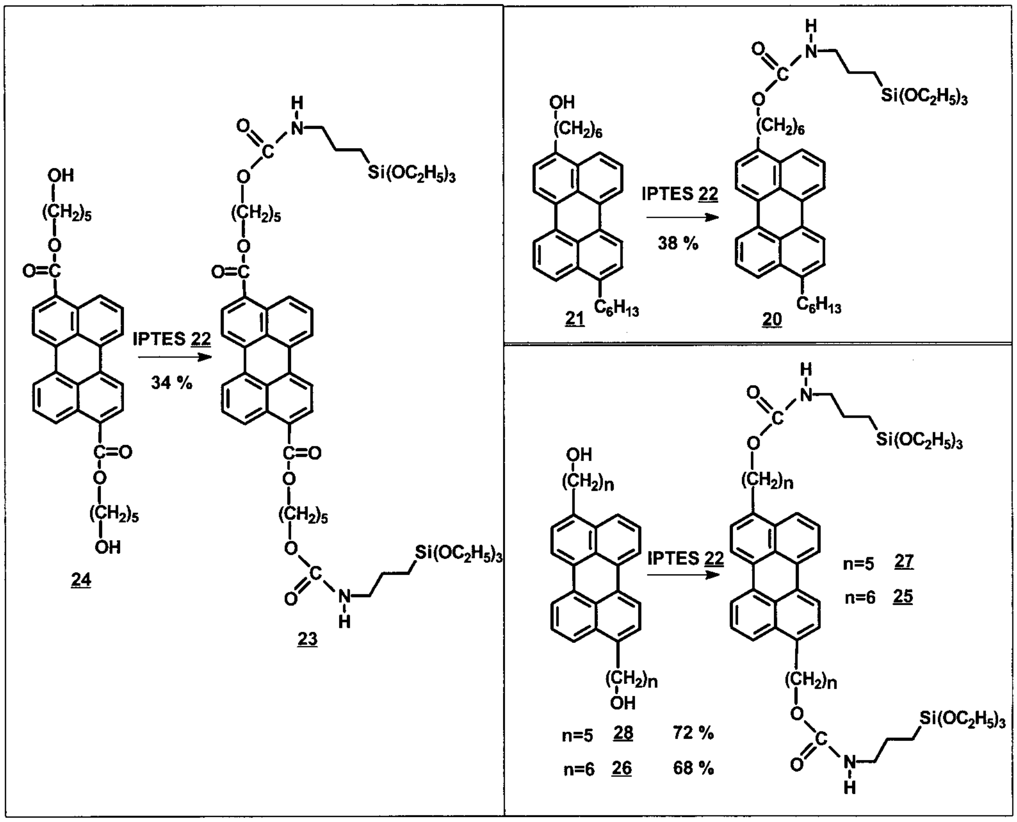
Scheme 3. Reaction of 3-Mono- or 3,9(10)-Bis(ω-hydroxyalkyl)perylene with (3-Isocyanatopropyl)triethoxysilane (IPTES) (22)



blue range of the visible spectrum. Moreover, the functional groups of these perylene derivatives allowed us to introduce alkoxysilanes and therefore to prepare yellow-colored matrixes by chemical attachment of the chromophore.

Using 3-mono- or 3,9(10)-bis(ω-hydroxyalkyl)perylenes (the mixture of the isomers 3,9- and 3,10-ω-dihydroxyalkylperylene could not be separated by column chromatography or HPLC[25]) reactions with (3-isocyanatopropyl)trialkoxysilane (IPTES) (**22**) led to the corresponding silane-modified derivatives (Scheme 3).

3,9(10)-Bis(ω-carboxyalkyl)perylenes, such as perylene **30**, could also be reacted with (3-isocyanatopropyl)triethoxysilane. The same product **29** was obtained if the reactive acid chloride **31** of perylene **30** was synthesized and finally reacted with aminoalkylsilanes such as APTES (**5**) (Scheme 4).

All synthesized 3,9(10)-substituted silane derivatives of perylene have a lower solubility (between 2 and 6 mg/mL) than the phenoxy-substituted perylenetetracarboxdiimides. However, their solubility sufficed to incorporate them homogeneously in the sol−gel process up to 3 wt %.

One problem arose in the synthesis of all silane-modified perylenes. The high susceptibility of alkoxy-substituted silanes toward nucleophilic substitution, for example, by water, especially in the presence of acid or base, limited the methods of purification of alkoxysilane-modified perylenes. Usually column chromatography over silica gel or aluminum oxide was used for purifying perylenes, but the silane derivatives of these dyes could react with the column material, as is obvious from Chart 3. Separation by GPC over polystyrene columns resulted in low yields, because most of the product remained on the columns. Therefore, the columns were also rendered useless. For that reason other methods of purification of the silane derivatives of perylene were tested. Recrystallization and/or washing processes led to purified derivatives which showed correct spectroscopic data except for some samples where the experimental values of the elemental analysis differed from the calculated ones. The values of C were decreased while the values of N were increased. This effect can be explained by physically adsorbed APTES or IPTES.[34] These physically adsorbed silanes could only be detected by NMR spectroscopy if they were present in large amounts. Analytically pure samples could be obtained by GPC or extensive washing processes which both led to a drastic reduction of the yield. Therefore, not all samples for analysis were purified by these methods, due to the fact that recrystallization and/or washing processes sufficed for the application of the dyes in the sol−gel process. The physical adsorption of silanes APTES and IPTES did not have any influence on the solubility and the optical properties of the perylene. Both APTES and IPTES behaved like the network-forming silanes (e.g., MTEOS) since they could also hydrolyze and co-condense with other alkoxysilanes. Therefore, they were integrated into the network. Because the ratio of physically adsorbed silanes to matrix-forming silanes was small, the mechanical properties of the matrix were also not changed.

To prevent the formation of too many side products, which could not be separated, the reaction conditions were chosen to be as mild as possible.

Scheme 4. Synthesis of Perylene 29 by Reaction of 3,9(10)-Bis(5-carboxypentyl)perylene (30) with IPTES (22) or via the Acyl Chloride 31 with APTES (5)

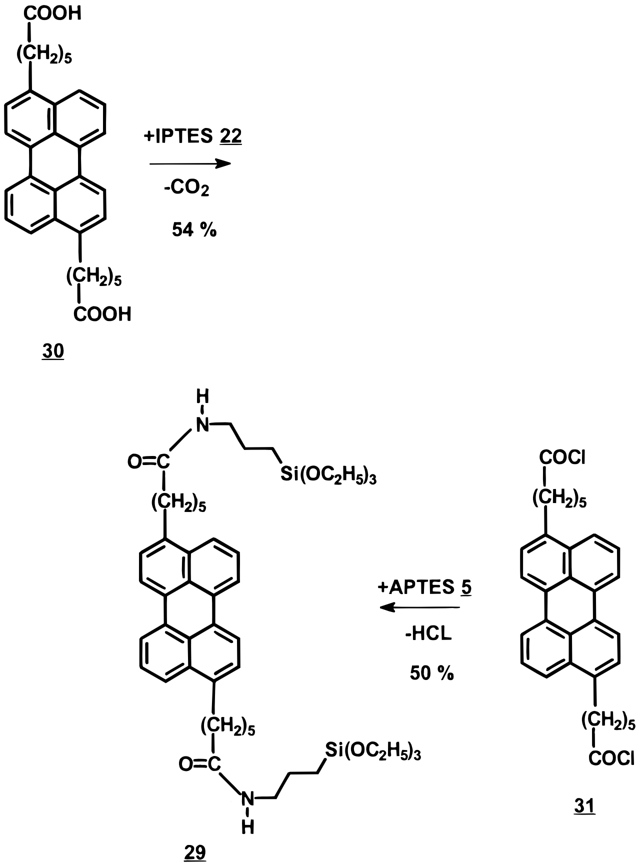
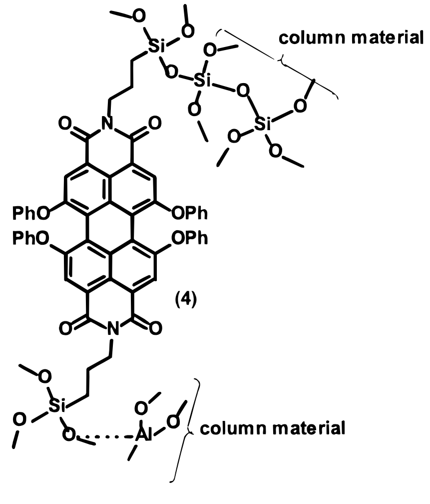


Chart 3. Reaction of Alkoxysilanes with the Column Material



Formulation of Sols. When sols are prepared, it is necessary to hydrolyze the alkoxysilanes which have to build up the network using water and a catalyst, for example, an acid. Besides temperature and dilution, factors determining the rate of the hydrolysis are the molarity and the molar relation of the catalyst to the alkoxy groups. Moreover, different alkoxysilanes show different reactivities toward hydrolysis. ^{29}Si NMR experiments prove that the silane derivatives of perylene require longer hydrolysis and condensation times in comparison to the network-forming silanes such as tetraethoxysilane (TEOS) or methyltriethoxysilane (MTEOS). This is due to the steric hindrance of the alkoxysilane-modified perylenes. Therefore, these chromophores were prehydrolyzed until some of their alkoxy groups turned into more reactive hydroxy groups which reacted with the alkoxy and hydroxy groups of the network-building silanes. The reaction conditions for the sol−gel process were chosen in such a way that a slow hydrolysis and condensation rate of the network-forming silane precursors resulted. Thus, the probability that the silane derivatives of perylene could be attached to the inorganic network was increased.

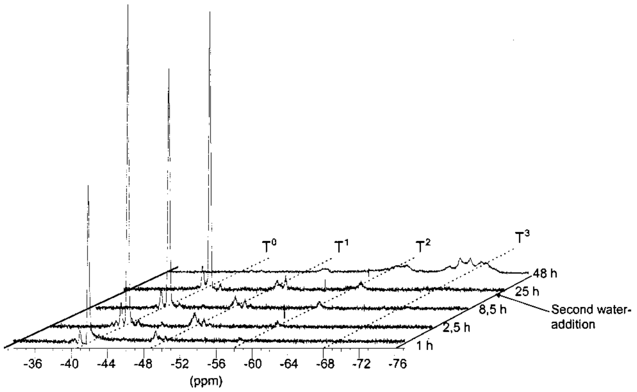


Figure 1. Reaction kinetics of the MTEOS−TEOS system, catalyzed with 0.1 N HCl (two-step addition, half-equimolar water amount), controlled by ^{29}Si NMR spectroscopy.

For the unfunctionalized perylenes, which were only physically admixed to the sols and could not react with the network by forming a covalent bond, the same reaction conditions were chosen, except that the prehydrolyzation was inapplicable. Therefore, there was the possibility of comparison between the matrixes doped with physically admixed perylenes and the matrixes doped with chemically attached perylenes.

The first system we developed was formed by TEOS and MTEOS in an equimolar ratio. These precursors which build an almost inorganic network are the best known and cheapest ones. For this system, we determined the optimal reaction conditions for incorporating the perylenes. A partial water addition (water addition in two steps, altogether to a half-equimolar stoichiometry) and an acid with low molarity were chosen. Both conditions caused a slow hydrolysis and condensation rate. In Figure 1 the kinetics of the MTEOS−TEOS sol, controlled by ^{29}Si NMR spectroscopy, is shown.

A sol which was suitable for film preparation was not reached before 48 h. After this reaction time the sol consisted mainly of T^2 and T^3 groups,[31] that is to say, highly condensed silanes. However, hydroxy groups still existed which were responsible for good adhesion to the substrate; e.g., they were able to connect to silicon on a glass substrate surface.

A comparison between sols doped with physically admixed perylenes and sols doped with the corresponding chemically incorporated perylenes showed that the latter are more homogeneous and more stable. The sols with chemically attached silane derivatives of perylene

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(31) T stands for three hydrolyzable groups, and Q stands for four hydrolyzable groups; The exponent gives information about the number of formed Si−O−Si linkages, i.e., the number of condensation reactions per molecule.

Table 3. Highest Available Concentrations of the Chemically and Physically Incorporated Perylene Derivatives in the MTEOS−TEOS Sol

perylene derivative	**3**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**23**	**25**	**27**	**29**
$c_{\max}$ by chemical incorporation of perylene (wt %)	0.5	<0.5	0.5	4	4	3	3	6	<3	3	3	3	3
corresponding perylene derivative	**32**	**32**	**33**	**34**	**35**	**37**	**38**	**36**	**39**	**39**	**39**	**39**	**39**
$c_{\max}$ by physical incorporation of the (corresponding) perylene (wt %)	n.d.	n.d.	n.d.	2	2	2	2	3	<1	<1	<1	<1	<1

Table 4. Highest Concentration of Perylene Derivatives 18 and 29 and Their Unfunctionalized Analogues 36 and 39, Reached in the DPSD and MPTS sols

perylene derivative, chemically attached	$c_{\max}$ (wt %) (DPSD−TEOS−GPTS sol)	$c_{\max}$ (wt %) (MPTS−Zr−GPTS sol)	perylene derivative, physically incorporated	$c_{\max}$ (wt %) (DPSD−TEOS−GPTS sol)	$c_{\max}$ (wt %) (MPTS−Zr−GPTS sol)
18	7	7.5	**36**	4	4
29	<4	<4.5	**39**	<1	<1

after storage for some days remained clear and homogeneous, while the analogous physically incorporated perylenes slowly precipitated. Additionally, the method of chemical attachment allows higher concentrations to be reached.

A complete list of the highest concentrations of the perylene derivatives incorporated in the MTEOS−TEOS sol is given in Table 3. The highest concentration here means the highest concentration of perylene in the sol which can be reached without perylene precipitating during storage.

To improve the solubility properties of the sol for the perylene dyes, especially for the silane derivatives of perylene that contain polar amino groups and urethane groups, we increased the polarity of the matrix by addition of (3-glycidoxypropyl)trimethoxysilane (GPTS); GPTS is an alkoxysilane which is organically modified with a polar group. The reaction conditions were analogous to those of the MTEOS−TEOS sol, with similar kinetics of both sols. Unfortunately, no improvement of the solubility could be reached.

Thereupon, we took into account that the perylene consists of an aromatic core, which could play a dominant role when the dye is incorporated into the sol−gel matrix. We developed a system which consisted of TEOS, GPTS, and diphenylsilane (DPSD). The phenyl groups cause a “touch of aromatic character” of the almost inorganic matrix and raise the flexibility of the network. ^{29}Si NMR investigations showed that the kinetics of the system were slower than those of the MTEOS−TEOS sol. The reason was probably the DPSD which condensed itself very slowly and rendered the condensation of the other silanes more difficult because of its bulky phenyl groups. The slow rate made addition of water in two steps unnecessary, so the water in a half-equimolar amount to the alkoxy groups was added in one step. In the final state of the sol, determined by ^{29}Si NMR spectroscopy, TEOS and GPTS were highly condensed, but DPSD was mainly present as a monomer. Also longer reaction times did not lead to a higher condensation of DPSD. The only possibility to polymerize DPSD was a prehydrolysis and precondensation at high temperatures, but then a homogeneous incorporation into the whole silane system was not successful. Because of the presence of DPSD monomer in large amounts, the synthesized sol led to films in which the DPSD recrystallized. The lower quality of these films made them unattractive for applications. However, we established that the concentration of incorporated perylenes could be increased, for both the physically admixed and the chemically attached perylenes. Again, the latter ones led to a more stable sol and higher concentrations. Values of concentrations for the most soluble perylene derivatives **18** and **29** are listed in Table 4.

For a further improvement of the solubility of perylene, we increased the flexibility of the inorganic network by using organically modified silane (GPTS and (3-methacryloxypropyl)trimethoxysilane (MPTS)) and introduced zirconium *n*-propoxide, a more reactive precursor than silanes. Zirconium is able to interact with aromatic systems[32] and with polar groups of the dye. It can also react as a complexing reagent, where Lewis acid−base interactions take place with the chromophore.[33]

During the synthesis of the GPTS−MPTS−Zr sol it appeared that the precursor zirconium *n*-propoxide showed a high tendency to react with water, precipitating as a heteropolysate of zirconium dioxide. Since this heteropolysate was not attached to the network, the sol became turbid and inhomogeneous. To prevent this reaction, it was necessary to increase the reactivity of zirconium alkoxide toward the silica network before the reaction with water occurred. Thus, MPTS was prehydrolyzed with 0.1 N HCl until the clearing point was reached, at which the two-phase mixture became one phase and the concentration of the hydroxy groups was at its maximum. At this time the zirconium alkoxide solution was added dropwise under an argon atmosphere and reacted immediately with the reactive hydroxy groups of MPTS. Zirconium dioxide was not formed under these conditions. The resulting sol was not moisture sensitive and was easy to handle.

While the unfunctionalized, physically admixed perylenes could only be incorporated in the same concentration as in the DPSD−GPTS−TEOS sol, the concentration of the alkoxysilane-modified perylenes was increased in the MPTS−Zr−GPTS sol, as shown in Table 4. This outcome can be attributed to the higher reactivity of zirconium *n*-propoxide in comparison to the alkoxysilanes. Thus, the zirconium precursor can covalently bind a larger amount of perylene molecules to the inorganic network.

Monolith Preparation. High vapor pressure caused by solvent in the sol and resulting capillary forces lead

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[32] Payne, K. L.; Puglishi, J. S. *J. Coat. Technol.* **1987**, *59*, 117.

[33] Guermeur, C.; Sanchez, C.; Schaudel, B.; Nakatani, K.; Delaire, J. A.; DelMonte, F.; Levy, D. *Proceedings of SPIE*, 30.07.-01.08; Sol−Gel-Optics IV, 1997; Vol. 3136, pp 10−19.

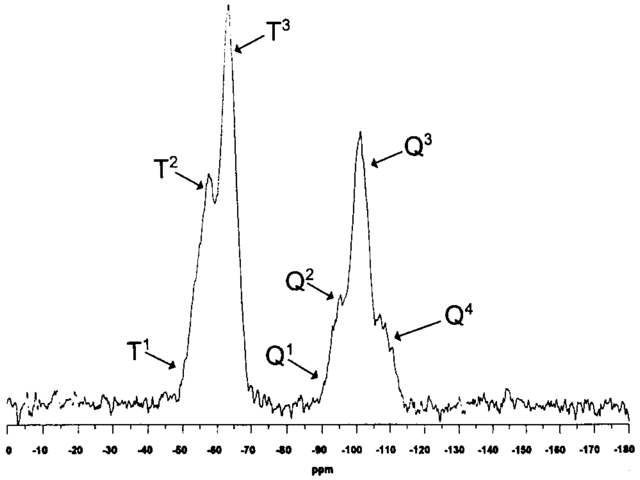

Figure 2. Solid-state ^{29}Si NMR spectrum of the cured MTEOS–TEOS (1:1) sol.

to a cracking of the monoliths,[34] so it was necessary to evaporate the solvent of the sols under a vacuum until highly viscous sols resulted. For each sol a suitable viscosity range was determined by a viscobalance. Additionally, a well-defined annealing process for each sol was developed which retards the condensation of the network, and thus, the solvent and the resulting water and alcohol have enough time to evaporate without causing cracking. Thereby each sol, having the suitable viscosity, was poured into a Teflon vessel, heated to a start temperature, and kept at this temperature until no weight loss was observed. Then the monoliths were heated to a higher temperature, and the procedure was repeated. The end temperature was attained when a higher temperature caused no weight loss. DSC measurements confirmed that no more reaction occurred. Temperatures up to 180 °C were used. Table 2 shows the determined temperature program for each sol.

Cleavage of the organic part of the inorganic–organic network is only observed at temperatures higher than 300 °C.[35,36] Therefore, at an end temperature of 180 °C the organic part was not burnt. By using solid-state and liquid ^{29}Si NMR spectroscopy,[37] a comparison of the states of the network before and after the annealing process becomes possible. The ^{29}Si NMR spectrum proves that further condensation reactions occur. Networks with mainly T^2, T^3 and Q^3, Q^4 groups[31] are formed, as shown by Figure 2. (The uncured system is shown in Figure 1; Figure 2 gives the spectra after 48 h).

Many experiments with different annealing programs have shown that too rapid heating to high temperatures (100 °C and higher) leads to a cracking of the monoliths. The reasons are strong capillary and inner tensions.[34]

Photostability. The photostability of various monoliths was investigated as a function of the concentration of the dyes, the type of incorporation of the dyes (physically or chemically), the composition of the host matrix, and the end temperature of the annealing process.

The photostability test was performed analogously to the standard method of the International Standard Organization (ISO).[22] It appears that the dye concentration plays no role. Also the variation of the sol composition led to no difference in the photostability of the incorporated dye. The photostability of dye-doped polymers can sometimes be improved by annealing the sample. Thus, after finishing the determined annealing program (Table 2), the monoliths were annealed at different temperatures from 120 to 200 °C for from one to several hours, resulting in no improvement of photostability. An annealing process at 200 °C even deteriorated the photostability of the monoliths.

A significant difference occurred between the monoliths with chemically attached perylene derivatives and those monoliths with analogous physically admixed chromophores: the perylene derivatives attached covalently to the matrix show a considerably higher photostability. Thus, *N*,*N*′-diisopropyl-1,6,7,12-tetrakis-(4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxyperylene-3,4:9,10-tetracarboxdiimide (**18**) was valued with the mark 4,[38] while the analogous silane derivative *N*,*N*′-bis(3-triethoxysilylpropyl)-1,6,7,12-tetrakis(4′-(1″,1″,3″,3″-tetramethylbutyl)phenoxyperylene-3,4:9,10-tetracarboxdiimide (**36**) received the mark 6.[38] This difference of the marks implies that, at lightening, the bleaching of the covalently attached dye took place 500 h later than the bleaching of the physically incorporated perylene. The significantly higher photostability of perylene **18** may be explained by the limitation of the rotational, vibrational, and translational degrees of freedom by covalent attachment of the dye to the matrix. Thus, the collision with other molecules that implies deactivating processes and decomposition processes can be minimized.[39] Moreover, the formation of aggregates is rendered more difficult, and therefore a photodegradation over the state of dye aggregates, as it is supposed for perylenes,[40] cannot take place.

Conclusions

Systematic examinations of structure–property relations showed not only that the composition of the sol–gel matrix and the structure of the dye should be matched but that the technique of incorporation of the dyes is also an important factor. Until now, perylene and peryleneimides could only be incorporated in sol–gel matrixes in low concentrations. A remarkable increase of dye concentration and a homogeneous incorporation were reached by the new method of modifying the perylene derivatives with alkoxysilanes, which enables their covalent attachment to the inorganic network during the sol–gel process. A further increase of the dye concentration was reached by suitable substitution in the *bay* position of perylene-3,4:9,10-tetracarboxdiimides. The best solubility was obtained with 1,1,3,3-(tetramethylbutyl)phenol as substituent.

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(35) Jonschker, G. Diploma thesis, University of Saarland, Saarbrücken, 1992.

(36) Kanziya, V. *J. Non-Cryst. Solids* **1990**, *121*, 182–187.

(37) Liquid ^{29}Si NMR experiments performed by Manfred Wagner, solid-state ^{29}Si NMR experiments performed by Markus Templin, group of Prof. Dr. Spiess, both at the Max-Planck-Institute for Polymer Research, Mainz.

(38) The valuation of the method, mentioned in ref 19: mark 4 means no bleaching after 100 h at lightening with a xenon lamp, mark 6 no bleaching after 600 at at lightening.

(39) Avnir, D.; Levy, D.; Reisfeld, R. *J. Phys. Chem.* **1984**, *88*, 5956–5959.

(40) Dr. A. Böhm, BASF AG, unpublished results.

Another important factor is the composition of the sol–gel matrix. Suitable variation of the precursors for formation of the inorganic network led to improved solubility properties of the matrix for the perylene dyes. The covalent attachment to the matrix led not only to higher concentrations and more homogeneous sols, but also to significantly better photostability.

These results make the sol–gel matrixes, doped with covalently attached perylenes, interesting materials for many applications. Novel luminescence diodes based on these sol–gel films have been examined.[41] Other applications for highly fluorescent, transparent, scratch-resistant films will be tested.

Acknowledgment. Support of this research by the Bundesministerium for Education and Research is gratefully acknowledged.

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(41) Schneider, M.; Hagen, J.; Haarer, D.; Müllen, K. Electroluminescent Devices Based on Perylene-Doped Sol–Gel Layers. *Adv. Mater.*, in press.