was heated again for 48 h at 100 °C. The pH adjustment and subsequent heating were repeated, and the precipitated MCM-41 product was collected by filtration. The product was washed with EtOH/HCl and calcined in air at 550 °C.

Pt/MCM-41: The calcined MCM-41 sample was slurried in a 3×10^{-3} wt% aqueous solution of $[Pt(NH_3)_4](NO_3)_2$ (Aldrich) for 3 h at room temperature to incorporate $[Pt(NH_3)_4]^{2+}$ ions into the channels of MCM-41 by exploiting the weak ion-exchange capability of the silica material. The solution-to-silica ratio was 100 mL g^{-1}. After this treatment, the sample was collected by filtration and subsequently dried in a vacuum oven at room temperature. The ion-exchanged Pt precursor was activated while being slowly heated to 320 °C in a stream of O_2 and then reduced with a stream of H_2 at 300 °C. The resultant sample contained 0.1 wt% Pt seed. This sample was immersed in 1.5×10^{-1} wt% aqueous solution of $[Pt(NH_3)_4(NO_3)_2]$, which corresponded to 5 wt% of the MCM-41 silica on the basis of Pt. After the solvent was completely evaporated in a rotary evaporator, the sample was further dehydrated in a vacuum oven at room temperature. The impregnated Pt-metal precursor was finally reduced in a stream of H_2 while the temperature was increased from room temperature to 300 °C over 4 h and maintained at 300 °C for 2 h. These treatments gave Pt nanowires inside the MCM-41 channels.

Unsupported Pt nanowires: A small amount of Pt/MCM-41 was added to a 10 wt% aqueous solution of HF diluted with ethanol. The silica was completely dissolved after stirring this solution gently at room temperature. The Pt nanowires were collected by filtration, washed with ethanol, and stored in ethanol until used.

TEM measurements: All samples (calcined MCM-41, Pt/MCM-41 and extracted Pt nanowires) were suspended in ethanol (99.9 vol%) by ultrasonication. The suspension was deposited on a carbon microgrid for TEM observation. The HREM observations were performed with a 400 kV electron microscope (JEM-4000EX) at room temperature. High-temperature observations were carried out by 1250 kV EM (JEM-1250) with a top-entry high-temperature stage.

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Network Polysilanes: Synthesis, Electrical Conductivity, Charge-Transfer Interaction, and Photoconductivity

Takanobu Kobayashi, Hirokazu Shimura, Shin Mitani, Saeko Mashimo, Aiko Amano, Toshihisa Takano, Minoru Abe, Hamao Watanabe,* Masashi Kijima, Hideki Shirakawa, and Hiroyuki Yamaguchi

Much attention has been paid to polysilanes because of their unique and versatile properties resulting from extensive delocalization of the σ electrons. These properties have made polysilanes useful as photoresists, ceramic precursors, photoconductors, semiconductors, and nonlinear optical materials in high technology fields.

With MeO-functionalized polysilanes as the starting material,[1] we recently obtained a new type of network polysilane, $[MeSi(OMe)_x(R)_y]_n$, with various R groups (alkyl, aralkyl, alkenyl, and aryl) as the side chains by the action of the corresponding Grignard reagents RMgX ($X = Cl, Br$).[2] Among these polysilanes, those having *N*,*N*-dialkylaminophenyl groups as side chains (p-$R'_2NC_6H_4$; $R' = Me$, Et, Pr) exhibited electrical conductivities on the order of 10^{-3} S cm^{-1} upon iodine doping; they are essentially stable under oxidative conditions because of their network structures.[2] Although linear polysilanes generally show high hole mobility or photorecepting ability due to their electrical characteristics,[3, 4] no studies regarding such properties for network polysilanes have appeared so far. This led us to study network polysilanes for applications as conducting materials when combined with organic electron acceptors such as 9,10-dicyanoanthracene (DCA), *p*-chloranil, and tetracyanoquinodimethane (TCNQ).

Studies on the preparation and properties of network polysilanes arising from Wurtz-type coupling reactions with alkylated trichlorosilanes as starting materials have appeared,[5] whereas there are only limited reports on arylated network polysilanes, which are accessible using the corresponding trichlorosilanes.[6] As part of a continuing study on network polysilanes, we now report on the properties, charge-transfer interactions with organic electron acceptors, photocarrier generation as well as electrical conductivity of two types of network polysilanes. The network polysilanes were prepared by homo- or copolymerization using arylated

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[*] Prof. Dr. H. Watanabe, T. Kobayashi, H. Shimura, S. Mitani, S. Mashimo, A. Amano, T. Takano, M. Abe
Department of Chemistry (Materials Science)
Faculty of Engineering, Gunma University
Gunma, Kiryu 376-8515 (Japan)
Fax: (+81) 277-30-1300
E-mail: hwatanab@chem.gunma-u.ac.jp

Prof. Dr. H. Shirakawa, Dr. M. Kijima
Institute of Materials, University of Tsukuba
Tsukuba, Ibaraki 305-8571 (Japan)

Dr. H. Yamaguchi
Department of Electronic Engineering, Gunma University
Gunma, Kiryu 376-8515 (Japan)

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trichlorosilanes (WZ-polysilanes) and the introduction of aryl groups into MeO-functionalized polysilanes (FR-polysilanes).

In contrast to the alkyltrichlorosilanes previously used,[5] the Wurtz coupling polymerization of arylated trichlorosilanes **1** proceeded readily with sodium under the usual conditions to give the corresponding soluble WZ-polysilanes **2** in reasonable to high yields. On the other hand, substituted MeO-functionalized network polysilanes **3** (FR-polysilanes) were obtained according to a previously reported method[2] (Table 1).

It was of interest to investigate the conductivity of polysilanes **2**, which have various groups as side chains, and to elucidate their spectral behavior by comparison with other polysilanes, since there have been only few reports describing the electrical conductivities of polysilanes.[2, 7] Thus, film samples of WZ-polysilanes **2a–i** and linear polysilanes **4a, b** were prepared on glass plates, and their conductivities were measured by the four-probe method using iodine as the dopant. Before doping, the values for all the polysilanes were on the order of $10^{-9}-10^{-7}\,\mathrm{S\,cm^{-1}}$. The values for the polysilanes **2c–h** bearing *N,N*-dialkylaminophenyl groups (*p*-$\mathrm{R'_2NC_6H_4}$; R′ = Me, Et) significantly increased upon doping to around 10^{-3} and then leveled off; these values remained unchanged for at least 15 h. This is comparable with the behavior of network FR-polysilanes bearing the same groups (**3c,d**).[2] In contrast, for the linear polysilanes **4a**, **b** and network polysilanes **2a, b, i** and **3b**, the conductivities only increased slightly upon doping (Table 1). The remarkable increase and the conductivities of **2c–h** may be due to the increased concentration of positive carriers, which are stabilized by the strong electron-donating nature of the *p*-$\mathrm{R'_2NC_6H_4}$ groups.

Table 2. Charge-transfer interactions between network polysilanes and organic electron acceptors and resulting absorption bands in $\mathrm{CH_2Cl_2}$.

Polysilane	λ_{max} [nm][b]			
(λ_{max} [nm])[a]	DCA	chloranil	TCNQ	iodine[c]
2b (none)	–[d]	–[d]	–[d]	none[e]
2c (287)	none[e]	none[e]	750, 850	362, 610(sh)
2d (288)	none[e]	none[e]	750, 850	364, 602(sh)
2e (280)	none[e]	none[e]	750, 850	362, 610(sh)
2f (285)	none[e]	none[e]	750, 850	360, 605(sh)
2g (273)	none[e]	none[e]	750, 850	363, 612(sh)
2h (278)	none[e]	none[e]	750, 850	362, 605(sh)
2i (none)	none[e]	none[e]	620, 750, 850	none[e]
3a (none)	none[e]	none[e]	600, 760, 850	none[e]
3b (none)	none[e]	none[e]	620, 750, 850	none[e]
3c (276)	none[e]	585	620, 750, 850	364, 602(sh)
3d (287)	none[e]	none[e]	620, 750, 850	364, 602(sh)
4a (335)	none[e]	–[d]	–[d]	–[d]
4b (330)	none[e]	–[d]	none[e]	362

[a] All the network polysilanes (**2b–3d**) exhibit, besides the peak noted, an absorption band rising near 400 nm, which increases in intensity with shorter wavelength. [b] The absoption intensities for these bands are fairly weak compared with those of the starting materials. [c] Absorption bands of solutions in dichloromethane prepared using the film samples after iodine doping. [d] Not determined. [e] Neither a color change nor an absorption peak were observed.

The enhanced conductivities are further supported by the spectral behavior in $\mathrm{CH_2Cl_2}$ of the film samples doped with iodine: Polysilanes **2c–h** and **3c, d**, which gave the higher conductivities, formed the corresponding charge transfer complexes ($\lambda_{max} = 365$ and 610(sh) nm, respectively; Table 2). Interestingly, the band in the 610 nm region, arising from the WZ-polysilanes doped with iodine, is in good agreement with that from the FR-polysilane **3c** and iodine ($\lambda = 615$ nm region),[2] which indicates that the two types of polysilanes have very similar structures. Therefore, the bands at $\lambda = 610$ nm from **2c–h** may correlate to the charge transfer complexes associated with their conductivities, as described for the FR-polysilanes.[2] Furthermore, it is likely that the smaller molecular weights do not significantly affect their conductivities and spectral properties,[8] particularly for **2d**, **i** compared with the other polysilanes (Table 1; see also Table 2).

Generally, the electrical conductivity of the polysilanes was determined by iodine doping because of the simple procedure. We have shown the first examples for the spectral observation of a charge-transfer interaction between network polysilanes having alkyl or aryl substituents and iodine.[2] We also found that in the DCA-photosensitized reaction of cyclopolysilanes

Table 1. Electrical conductivities of network polysilanes upon doping with iodine.

Starting materials	Polysilane	Yield [%]	$\bar{M}_w \times 10^{-3}$[a]	σ [S cm^{-1}][b]	
				before doping	after doping
$\mathrm{C_6H_{13}SiCl_3}$ (**1a**)	**2a**	89	20.0	5×10^{-9}	8×10^{-9}
$\mathrm{C_6H_5SiCl_3}$ (**1b**)	**2b**	60	5.4	3×10^{-8}	4×10^{-8}
p-$\mathrm{Me_2NC_6H_4SiCl_3}$ (**1c**)	**2c**	46	5.6	8×10^{-7}	5×10^{-3}
p-$\mathrm{Et_2NC_6H_4SiCl_3}$ (**1d**)	**2d**	53	3.3	5×10^{-7}	4×10^{-3}
1c + **1a**	**2e**	30	9.1	1×10^{-7}	9×10^{-4}
1d + **1a**	**2f**	22	12.4	2×10^{-7}	4×10^{-3}
1c + **1e**	**2g**	20	17.5	1×10^{-7}	1×10^{-3}
1d + **1e**	**2h**	20	9.7	4×10^{-7}	1×10^{-3}
1c + **1e**	**2i**	52	3.9	6×10^{-8}	4×10^{-7}
$[\mathrm{MeSi(OMe)}_l]_m$ (**1f**)[2] + $\mathrm{C_6H_{13}MgCl}$	**3a**	–	20.0	–	–
1f + 2-$\mathrm{SC_4H_3MgBr}$	**3b**	–	19.5	8×10^{-8}[c]	5×10^{-7}[c]
1f + *p*-$\mathrm{Me_2NC_6H_4MgBr}$	**3c**	–	18.5	2×10^{-7}[c]	1×10^{-3}[c]
1f + *p*-$\mathrm{Et_2NC_6H_4MgBr}$	**3d**	–	10.8	8×10^{-8}[c]	1×10^{-3}[c]
$\mathrm{C_6H_5MeSiCl_2}$ (**1e**)	**4a**[d]	–	24.0	4×10^{-8}	1×10^{-6}
$\mathrm{Cl(C_6H_5MeSiSiMe_2)Cl}$ (**1g**)[14]	**4b**[d,e]	–	348.0	1×10^{-7}	3×10^{-6}

[a] Determined by gel permeation chromatography (GPC) with polystyrene standards. [b] The electrical conductivity σ was measured with a film on a glass plate by the four-probe method at room temperature. [c] Taken from ref. [2]. [d] Prepared according to the present method (see Experimental Section). [e] Available from Yuki Gosei Kogyo Co. Ltd.; prepared according to ref. [14] using monomer $\mathrm{ClMePhSiSiMe_2Cl}$.

$[R_2Si]_n$ ($n = 3-7$, R = alkyl; $\lambda_{max} = 250-300$ nm) electron transfer only occurs from the cyclosilanes to DCA (the longest wavelength absorption band is at $\lambda_{max} = 425$ nm) upon irradiation with light ($\lambda > 390$ nm), producing the DCA anion radical as the intermediate.[9] Thus, to obtain information about the charge-transfer interactions between network polysilanes and organic electron acceptors such as DCA ($E_{1/2} = -0.97$ V),[10] p-chloranil ($E_{1/2} = -0.92$ V),[10] and TCNQ ($E_{1/2} = -0.45$ V; all values with respect to the standard calomel electrode (SCE)),[10] we carried out a series of spectral measurements, because this would disclose a useful property of the network polysilanes as photoconducting materials.

Upon mixing network polysilanes **2c**–**h** and **3a**–**d** with DCA or chloranil in CH_2Cl_2, the solutions showed, based on their absorption spectra, neither an interaction nor formation of a charge-transfer complex, except in the case of **3c** with chloranil, where the charge-transfer complex was formed ($\lambda_{max} = 585$ nm, blue color; Table 2). Equally, in experiments using TCNQ, WZ-polysilanes **2c**–**h** only formed the TCNQ anion radical[11] ($\lambda_{max} = 750$, 850 nm; green), whereas with the FR-polysilanes **3a**–**d** both the complex ($\lambda_{max} = 600-620$ nm) and the TCNQ anion radical resulted ($\lambda_{max} = 750$, 850 nm; blue-green). However, the combination of the two types of network polysilanes and iodine ($E_{1/2} = -0.57$ V)[10] resulted in the formation of only charge-transfer complexes ($\lambda_{max} = 362-364$, $602-610$ nm (sh)) except for **2b, i** and **3a, b** (Table 2). In the ESR spectral analysis in CH_2Cl_2, a solution ($\lambda_{max} = 364$, 602 nm (sh)) consisting of polysilane **3c** and iodine as well as DCA or chloranil exhibited no signal, while similar experiments for a sample from **3c** and TCNQ afforded a signal due to the TCNQ anion radical. These results clearly show that in almost all cases the network polysilanes **2c**–**h** and **3a**–**d** do not interact with DCA or chloranil, which have higher reduction potentials. In contrast, with iodine or TCNQ, which have lower reduction potentials or stronger electron-accepting abilities, they form the corresponding charge-tranfer complexes and/or TCNQ anion radicals. Thus, it can be concluded that the oxidation potentials for the series of polysilanes[12] decrease in the following order: **2c**–**2h** < **3c**, **3d** < **3a**, **3b** ≅ **2i** < **4a**, **4b**; that is, the reducing ability or electron-donating nature of the polysilanes decreases in this order. These results, together with those of the previous study on the DCA-photosensitized reaction,[9] provide quite helpful information with respect to the photoconductivity in WZ- and FR-polysilane systems.

To clarify the photoconductivity of the polysilanes, we have qualitatively investigated the generation of the carrier by means of transient photoconductivity analysis using single-layer films consisting of network polysilanes (ca. 42% in weight), DCA (ca. 8%) as a sensitizer, and polybutyral (ca. 50%) as a phototransparent binder. Film samples were irradiated with a field strength on the order of 10^4 V cm^{-1} using a pulsed laser light (10 ns, $\lambda = 425$ nm, 1 mJ cm^{-2} per pulse) which coincides with the longest wavelength absorption band of DCA at $\lambda = 425$ nm. Irradiation of control samples containing only polysilane (50%) in polybutyral (50%) showed no signal, and samples consisting of DCA (50%) and polybutyral (50%) produced only very weak signals (mV in intensity) due to carrier generation (Figure 1a). Interestingly enough, upon irradiation samples similarly prepared with selected WZ- and FR-polysilanes produced signals due to the carrier concentration which were enhanced by one order of magnitude compared with the control samples. The intensities of the observed signals remained unchanged during irradiation in each case, but upon conclusion of irradiation the signals immediately disappeared. The signal for the hole carrier arising from the sample consisting of **3c** and DCA is shown as an example in Figure 1b. Based on these results, it was evident that both the WZ- and FR-polysilanes bearing the aryl group would be useful for use as new photoconducting materials consisting of stable silicon network structures. As has been shown in studies on the photoconductivities of linear polysilanes[4c,d,e] and silicon-based polymers,[13] it is likely that generation of the carrier by electron transfer from polysilanes to the photoexcited DCA efficiently results in hole transport between the polysilanes in the present single-layer systems.

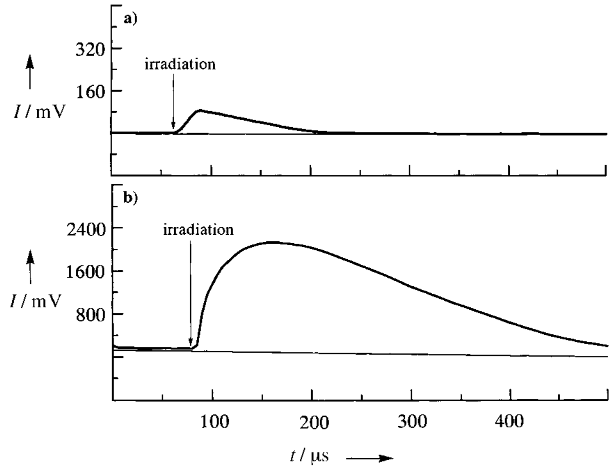

Figure 1. Carrier signals generated by one-time irradiation (10 ns) with pulsed laser light at $\lambda = 425$ nm for a) a control sample of DCA (50% by weight) in polybutyral (50%; film thickness 20 µm) and b) a sample containing polysilane **3c** (42%), DCA (8%), and polybutyral (50%; film thickness 6 µm). The termination of irradiation results in a base-line signal in each case. I = intensity.

Finally, it should be stressed that, as expected from the FR-polysilanes,[2] the WZ-polysilanes are capable of forming stable films after doping with iodine because of the resulting network structures. Furthermore, polysilanes **2c**–**h**, bearing the strong electron-donating groups, showed constant and stable electrical conductivities on the order of 10^{-3} S cm^{-1}, even after standing for at least 15 h. From the combination of the WZ- or FR-polysilane donor and DCA acceptor, qualitative evidence for the carrier generation followed by efficient hole transport was obtained for the first time by irradiation at $\lambda = 425$ nm with pulsed laser light. Therefore, the present results open up the way for new applications for the two types of network polysilanes as photoconducting materials. In addition, the synthesis of donor–acceptor systems resulting from the interaction between organic electron acceptors such as DCA, chloranil, and TCNQ, which have different reduction potentials, and various polysilanes provide a convenient method for the estimation of the electron-donating ability of polysilanes using electronic absorption spectroscopy in solution.

Experimental Section

As an example, the synthesis of **2a** is described: A solution containing *p*-*N*,*N*-dimethylaminophenyltrichlorosilane (**1c**; 1.27 g, 5 mmol) and hexyltrichlorosilane (**1a**. 1.11 g, 5 mmol) in HMPA (2 mL) was added dropwise with high-speed stirring and toluene refluxing within 15 min to a sodium dispersion (0.84 g, 36 mmol) prepared in refluxing toluene (30 mL). The mixture was stirred for 2 h with refluxing, treated with MeLi (ca. 1.2 mL of a 1.1M solution in diethyl ether) at 50 °C for 1 h, and cooled. The excess Na was quenched with MeOH, and the resulting mixture was washed with water. The toluene solution obtained was dried over $MgSO_4$ and evaporated under reduced pressure to give the crude products which were dissolved in THF. Fractional precipitation obtained by pouring the THF solution onto *i*PrOH gave a precipitate which was collected on a filter and dried to give **2e** as a pale yellow powder (0.373 g; 30 % Si yield based on the starting materials) as a methanol-insoluble and toluene-soluble material ($[p\text{-}(Me_2NC_6H_4Si)_{0.48}(C_6H_{13}Si)_{0.52}]_n$; $M_w = 9100$). The reactions for the other chlorosilanes were carried out in a similar manner to give the corresponding products **2**. The products were characterized by IR, NMR, and UV/VIS spectroscopy, and the relative molecular weights M_w were determined. Polysilanes **2c–h** showed a UV/Vis absorption peak at $\lambda = 280$ nm linked to the curve rising near $\lambda = 400$ nm that increases in intensity with shorter wavelength, suggesting that the structure is a network system[15] to which the hexyl and aryl side chains are attached. Thermogravimetric analyses of the polysilanes **2a–i** (40–1000 °C, heating rate 10 °C min^{-1}, N_2 stream) were carried out; the weight losses were less than 5% at 300 °C for all samples tested, except for **2c**. Molecular weight and spectral data for the polysilanes: **2a**: $(C_6H_{13}Si)_n$, $M_w = 21400$, $M_w/M_n = 3.3$; ^1H NMR ($CDCl_3$): $\delta = 0.5–2.3$ (SiC_6H_{13}, 13.0 H). **2b**: $(PhSi)_3$, $M_w = 3200$, $M_w/M_n = 1.8$; ^1H NMR ($CDCl_3$): $\delta = 5.3–8.5$ (SiC_6H_5, 5.0 H). **2c**: $(p\text{-}Me_2NC_6H_4Si)_n$, $M_w = 4400$; $M_w/M_n = 1.2$; ^1H NMR ($CDCl_3$): $\delta = 2.2–3.3$ (NCH_3, 6.0 H), 5.1–8.0 (C_6H_4, 4.0 H). **2d**: $(p\text{-}Et_2NC_6H_4Si)_n$, $M_w = 3300$, $M_w/M_n = 1.2$; ^1H NMR ($CDCl_3$): $\delta = 0.6–1.4$ ($NCCH_3$, 6.0 H), 2.5–3.6 (NCH_2C, 4.0 H), 5.3–7.9 (C_6H_4, 4.0 H). **2e**: $[(p\text{-}Me_2NC_6H_4Si)_{0.35}(Hex\text{-}Si)_{0.65}]_n$, $M_w = 14300$. $M_w/M_n = 1.6$; ^1H NMR ($CDCl_3$): $\delta = 0.2–2.0$ (C_6H_{13}, 25.3 H), 2.5–3.1 (NCH_3, 6.0 H), 6.0–7.7 (C_6H_4, 3.9 H). **2f**: $[(p\text{-}Et_2NC_6H_4Si)_{0.30}(HexSi)_{0.70}]_n$, $M_w = 12400$, $M_w/M_n = 1.4$; ^1H NMR ($CDCl_3$): $\delta = 0.1–2.0$ ($C_6H_{13}Si$, 27.3 H, $NCCH_3$, 6.0 H), 2.7–4.2 (NCH_2, 4.0 H), 6.2–8.3 (C_6H_4, 4.0 H). **2g**: $[(p\text{-}Me_2NC_6H_4Si)_{0.45}(MePhSi)_{0.55}]_n$, $M_w = 5000$, $M_w/M_n = 1.2$; ^1H NMR ($CDCl_3$): $\delta = -0.8–0.8$ ($SiCH_3$, 4.5 H), 2.4–3.7 (NCH_3, 6.0 H), 6.2–8.1 (C_6H_4, 4.0 H; C_6H_5, 7.0 H). **2h**: $[(p\text{-}Et_2NC_6H_4Si)_{0.45}(MePhSi)_{0.55}]_n$, $M_w = 9700$, $M_w/M_n = 1.2$; ^1H NMR ($CDCl_3$): $\delta = -0.9–0.8$ ($SiCH_3$, 4.0 H), 0.8–2.0 ($NCCH_3$, 6.0 H), 2.7–3.9 (NCH_2C, 4.0 H), 5.9–8.1 (C_6H_4, 4.0 H; C_6H_5, 6.6 H). **2i**: $[(p\text{-}Me_2NC_6H_4Si)_{0.04}(MePhSi)_{0.96}]_n$, $M_w = 3900$; ^1H NMR ($CDCl_3$): $\delta = -1.0–0.8$ ($SiCH_3$, 3.0 H), 2.6–3.1 (NCH_3, 0.25 H), 6.1–7.7 (C_6H_4, 0.17 H; C_6H_5, 5.0 H).

The synthesis of **3a** from MeO-functionalized polysilane $[MeSi(OMe)_l]_m$ (**1f**; $M_w = 24000$, $M_n = 4400$; $l = 0.4$)[2] by a Grignard alkylation is described as a typical example: A solution of $C_6H_{13}MgCl$ (12.3 mmol) was prepared from magnesium and hexyl chloride in THF (10 mL). The Grignard reagent was added with stirring to a solution containing polysilane **1f** (0.50 g) in THF (10 mL). After a weakly exothermic reaction, the mixture was heated at 40 °C for 20 h with stirring, and then dry methanol (2–3 mL) was added to quench the active species. From the resulting mixture, the solvent was removed completely to give a solid material, which was extracted with toluene (ca. 50 mL). The toluene extracts were concentrated under reduced pressure, and warm methanol (15 mL) was added to precipitate a solid material, which was collected on a filter, washed with methanol, and then dried under reduced pressure. The obtained FR polysilane **3a** was a pale yellow powder ($[MeSi(OMe)_{0.18}(Hex)_{0.23}]_n$, $M_w = 20000$, $M_n = 4300$; 0.54 g, 108 % yield based on **1f**.[2] The other FR-polysilanes (**3b–d**) were prepared in a simialar manner (see Table 1). Products **3a–d** were identified and characterized as previously described[2] (see also the WZ-polysilanes and footnote [b] in Table 2). Molecular weight and spectral data for the four polysilanes: **3a**: $[MeSi(OMe)_{0.18}(Hex)_{0.23}]_n$, $M_w = 20000$, $M_w/M_n = 4.6$; ^1H NMR ($CDCl_3$): $\delta = -0.5–0.7$ ($SiCH_3$, 3.0 H; $SiCH_2C_5$, 0.2 H), 0.8–1.0 (C_4CH_3, 0.7 H), 1.1–1.6 ($SiC(CH_2)_4C$, 1.8 H), 3.2–3.8 ($SiOCH_3$, 0.6 H). **3b**: $[MeSi(OMe)_{0.21}(SC_4H_3)_{0.08}]_n$, $M_w = 9500$, $M_w/M_n = 3.1$; ^1H NMR ($CDCl_3$): $\delta = -0.4–1.0$ ($SiCH_3$, 3.0 H), 3.0–3.6($SiOCH_3$, 0.6 H), 7.0–7.8 (SC_4H_3, 0.3 H). **3c**: $[MeSi(OMe)_{0.21}(C_6H_4NMe_2)_{0.22}]_n$, $M_w = 8700$, $M_w/M_n = 3.2$; ^1H NMR ($CDCl_3$): $\delta = -0.2–1.0$ ($SiCH_3$, 3.0 H), 2.7–3.1 (NCH_3, 1.3 H, $SiOCH_3$, 0.6 H), 6.5–7.6 (C_6H_4, 0.9 H). **3d**: $[MeSi(OMe)_{0.23}(C_6H_4NEt_2)_{0.29}]_n$, $M_w = 9900$, $M_w/M_n = 2.9$; ^1H NMR ($CDCl_3$): $\delta = -0.2–0.9$ ($SiCH_3$, 3.0 H), 1.0–1.3 ($NCCH_3$, 1.8 H), 3.0–3.7 (NCH_2C, 1.2 H; $SiOCH_3$, 0.7 H), 6.4–7.6 (C_6H_4, 1.2 H).

Preparation of the sample films for measurement of electrical conductivity: A solution containing the polysilane (ca. 50 mg) in solvent (0.5 mL; toluene, xylene, or DME) was prepared. The sample films (thickness 10–40 µm; area size ca. 16 mm × 9–12 mm) were prepared by spin-coating the solution on a glass plate (18 mm × 18 mm) and dried for 1 h at about 60 °C. The glass plate was equipped with four gold-film electrodes at regular intervals of 2 mm prior to the spin-coating, and fine leading wires were attached to the four gold electrodes. For the electrical conductivity measurement, the sample film thus obtained was placed in an apparatus, which was equipped with a programmable DC voltage/current generator TR-6142 (ADVANTEST Co. Ltd.), digital electrometer TR-8652 and computing digital multimeter TR-8651 (Takeda Scientific Laboratories Co. Ltd.), and GP-IB adapter (ADVANTEST Co. Ltd.), and after evacuation the electrical conductivity (σ [S cm^{-1}]) of the sample was measured at 20 °C by a typical four-probe method before and after doping with saturated iodine vapor.

Preparation of sample films for the photoconductivity measurement: The sample films (thickness 5–25 µm; area size ca. 10 × 10 mm) were prepared on a conducting glass plate[16] by spin-coating with a solution prepared by mixing polysilane in CH_2Cl_2 with DCA and phototransparent polybutyral in CH_2Cl_2, and then drying at about 60 °C for 1 h. Fine leading wires for the three electrodes were attached to the sample film, on which a gold-film electrode was placed by evaporation in vacuo, and on the conducting film of the plate on both sides across the sample film. The measurement for the signals due to the photocarrier generation in the single layer films is described in the text.

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Synthesis, Structure, and Magnetism of a Novel Alkoxide Bridged Nonacopper(II) (Cu_9O_{12}) [3 × 3] Square Grid Generated by a Strict Self-Assembly Process[**]

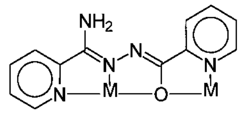
Liang Zhao, Zhiqiang Xu, Laurence K. Thompson,[*]
Sarah L. Heath, David O. Miller, and Masaaki Ohba

Single ligands with repeating linear arrays of coordination pockets have the potential to create gridlike arrangements of metal centers by self-assembly processes. Linear polytopic ligands of this sort with pyridazine and pyrimidine bridging subunits have produced essentially flat [2 × 2] homotetranuclear grids with Cu^I and Co^{II} salts,[1, 2] and a flat [3 × 3] nonanuclear grid with Ag^I salts.[3]

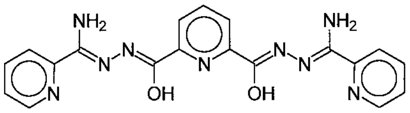
The Co^{II} complex has been shown to exhibit antiferromagnetic coupling within the cluster, despite long distances of separation between the metal centers (6.5 Å).[4] The ordering of paramagnetic metal ions in gridlike arrays presents the possibility of extended spin communication within a lattice of closely spaced metal ion centers, generated from a single preprogrammed ligand. The nuclearity of these clusters is clearly based on the polytopic nature of the ligand and the ability of the metal to read and interpret the coordination options presented by the ligand in the most efficient way, depending on its own coordination algorithm.[3]

Tetradentate ligands (e.g. poap) built on a flexible diazine (N–N) backbone have been shown to self-assemble Mn^{II}, Co^{II}, Ni^{II}, and Cu^{II} centers into square, tetranuclear clusters, with just alkoxide bridges between the metal ions.[5] These systems have close metal–metal spacings (≈4 Å) and display dominant antiferromagnetic intramolecular exchange, except in the copper(II) cases where ferromagnetic coupling, associated with orthogonal magnetic connections, prevails. Spin-coupled, homoleptic trigonal-bipyramidal alkoxo-bridged Mn^{II}_5[6] and Co^{II}_5[7] clusters have also been produced, in which there is an exact match between the ligand donor pocket groupings and the coordination requirements of the six-coordinate metal centers.

Extension of poap using a 2,6-disubstituted pyridine central fragment generates the ligand 2poap, which has an approximately linear array of coordination pockets that produce five-membered chelate rings on coordination. The ligand 2poap behaves as a nonadentate ligand in reaction with copper(II) acetate, producing a linear trinuclear complex **1**, in which a central copper center is bound to the other copper centers through N–N diazine single bond bridges.[7] However with copper(II) nitrate and copper(II) sulfate 2poap behaves as a heptadentate ligand, providing donors for nine metal coordination sites through oxygen bridging, and nonanuclear complexes are formed in both cases. Reaction of 2poap with $Cu(NO_3)_2 \cdot 3H_2O$ in water produced a brown crystalline product **2** (71% yield), suitable for structural analysis.[8] A similar reaction with $CuSO_4 \cdot 5H_2O$ produced the dark green crystalline product **3** (75% yield).[7]



poap



2poap

$[Cu_3(2poap\text{-}2H)CH_3COO)_4] \cdot 3H_2O$ **1**

$[Cu_9(2poap\text{-}H)_6](NO_3)_{12} \cdot 9H_2O$ **2**

$[Cu_9(2poap\text{-}H)_6](SO_4)_6 \cdot 18H_2O$ **3**

The structure of **2** (Figure 1) involves a novel [3 × 3] grid of nine pseudo-octahedral Cu^{II} centers coordinated by two groups of three roughly parallel ligands arranged above and below the metal pseudo-plane, with the metals bridged just by alkoxide oxygen atoms. The ligands are roughly eclipsed, but have a slight stagger. The parallel grouping of the ligands is associated with π interactions between the aromatic rings (ring separations ≈3.6–4.2 Å). Three different pseudo-octahedral copper(II) centers are found; the central Cu atom has a

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[*] Prof. L. K. Thompson, L. Zhao, Z. Xu, D. O. Miller
Department of Chemistry
Memorial University of Newfoundland
St. John's, NF, A1B 3X7 (Canada)
Fax: (+1) 709-737-3702
E-mail: lthomp@morgan.ucs.mun.ca

Dr. S. L. Heath
Department of Chemistry
University of York
Heslington, York, YO10 5DD (UK)

Dr. M. Ohba
Department of Chemistry
Faculty of Science
Kyushu University 33
Hakozaki, Higashi-Ku, Fukuoka 812 (Japan)

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