2,3-Tetrakis[4-(*N*-2-naphthyl-*N*-phenylamino)phenoxy]-substituted Metal-free and Metal Phthalocyanines as a Novel Class of Amorphous Molecular Materials

Martin Ottmar, Toshiki Ichisaka, L. R. Subramanian,† Michael Hanack,† and Yasuhiko Shirota*
Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565-0871
†*Institut für Organische Chemie, Fakultät für Chemie und Pharmazie, Universität Tübingen, D-72076 Tübingen, Germany*

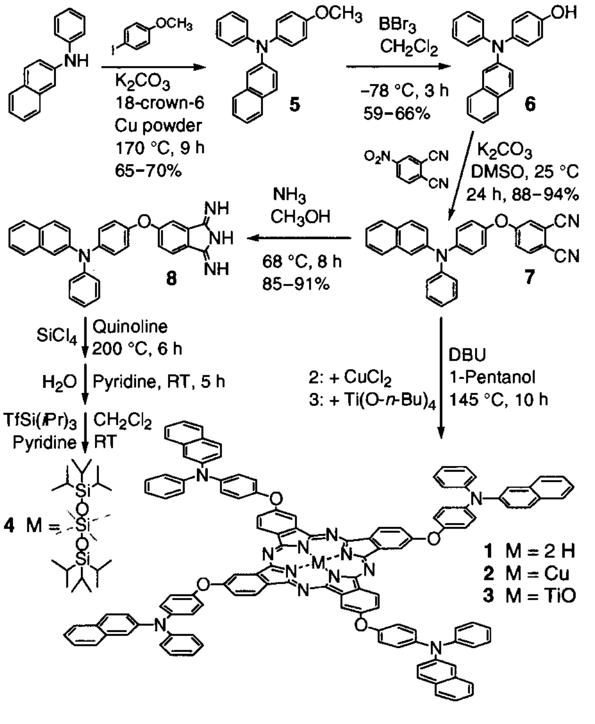
(Received May 11, 2001; CL-010436)

A novel family of metal-free and metal phthalocyanines containing triarylamine moieties are synthesized. These compounds are well soluble and readily form stable amorphous glasses with high glass transition temperatures, as evidenced by differential scanning calorimetry and X-ray diffraction, and constitute a new class of amorphous molecular materials.

Actual applications usually require materials as solids. Hence, the solid state morphology of candidate materials and control over it is of great interest in materials science. The inevitable presence of grain boundaries in polycrystalline materials can affect the performance of electronic and optoelectronic devices due to possible electric short circuits or light scattering. By contrast, amorphous molecular materials have recently demonstrated their suitability and versatility in a number of roles in organic optoelectronic devices.[1] We report here the creation of a novel class of amorphous molecular materials containing phthalocyanine cores. Phthalocyanines have seen more than sixty years of active scientific pursuit and refinement from a class of simple pigments into functional materials for a wide range of purposes.[2] However, they are generally crystalline and many are also insoluble in organic solvents. It is therefore of both fundamental and technological interest to develop soluble and amorphous glass-forming phthalocyanines with high glass transition temperatures (T_gs). To our best knowledge, known examples of such phthalocyanines are very scarce and have comparatively low T_gs.[3]

In this study, four new, soluble phthalocyanines that readily form stable amorphous glasses with high T_gs were synthesized, comprising 2,3-tetrakis[4-(*N*-2-naphthyl-*N*-phenylamino)phenoxy]phthalocyanine **1**, 2,3-tetrakis[4-(*N*-2-naphthyl-*N*-phenylamino)phenoxy]phthalocyaninato copper **2**, 2,3-tetrakis[4-(*N*-2-naphthyl-*N*-phenylamino)phenoxy]phthalocyaninato titanium oxide **3** and 2,3-tetrakis[4-(*N*-2-naphthyl-*N*-phenylamino)phenoxy]phthalocyaninato bis(triisopropylsiloxy)silicon **4**. These compounds constitute a new class of phthalocyanines whose molecular architecture differs significantly from that of previously reported ones.

1–**4** were synthesized as shown in Scheme 1. *N*-Phenyl-2-naphthylamine was treated with 4-iodoanisole in the presence of potassium carbonate, 18-crown-6 ether and copper powder to give *N*-(4-methoxyphenyl)-*N*-phenyl-2-naphthylamine **5**, which was deprotected to the free phenol **6** with boron tribromide in dry dichloromethane under nitrogen at –78 °C, and subsequently reacted with 4-nitrophthalonitrile in DMSO in the presence of potassium carbonate to give the phthalocyanine precursor **7**. **1**–**3** were synthesized directly from **7** in 1-pentanol catalyzed by 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). For **2** and **3**, anhydrous copper chloride and titanium tetra-*n*-butoxide served as metal sources. **1** also forms as a by-product of **3** in low yield. For the synthesis of **4**, **7** was treated with ammonia in methanol to give the isoindolenine **8**, which was condensed to the corresponding dichlorosilicon phthalocyanine with silicon tetrachloride in quinoline. After hydrolysis to its dihydroxy analogue, reaction with triisopropylsilyl triflate in dichloromethane and pyridine gave **4**. **1**–**4** were all obtained as mixtures of the four constitutional isomers that normally form during synthesis of 2,3-tetrasubstituted phthalocyanines due to statistical orientation of the 4-substituted precursor nitrile in yields shown in Table 1. Scheme 1 shows only the most symmetrical C_{4v} isomer. The isomers' existence alone generally does not prevent the formation of crystalline solids despite contributing to solid state disorder.[2]



Scheme 1.

1–**4** were purified by silica-gel column chromatography. Precipitation from dichloromethane with excess methanol gave turquoise (**1**, **2**) or green powders (**3**), while solvent evaporation to dryness afforded dark blue or dark green flakes. **4** could not be precipitated with methanol and was obtained as blue flakes with a violet sheen. **1**–**4** were identified by various spectroscopic methods, mass spectrometry and elemental analysis.[4]

The four synthesized new phthalocyanines were obtained as amorphous solids despite attempted crystallization from solution. Their amorphous glassy state was evidenced by polarized light microscopy, X-ray diffraction (XRD) and differential scan-

Copyright © 2001 The Chemical Society of Japan

Table 1. Yields, glass transition temperatures and electronic absorption data of the synthesized phthalocyanine

Pc	Yield / %[a]	T_g / °C	UV Maxima λ_{max} /nm (Molar Extinction Coefficients ε / 10^5 $M^{-1}cm^{-1}$)[b]			
1	31	128	280 (1.58)[c]	322 (1.95)[c, d]	608[e], 641[e]	668 (1.73)[f], 702 (2.01)[f]
2	60	149	280 (1.38)[c]	322 (1.50)[c, d]	614[e]	682 (1.99)[f]
3	23	172	280 (1.39)[c], 320 (1.49)[c]	348 (1.25)[d]	633[e]	704 (2.32)[f]
4	24	122	281 (1.13)[c], 322 (1.24)[c]	356 (1.14)[d]	615[e]	684 (2.33)[f]

[a]Based on **7** for **1–3** and **8** for **4**. [b] All spectra were taken in dichloromethane. [c]Arylamine system (**5**: λ_{max} 280 (0.29), 313 (0.29), 364 (0.03)). [d]Soret band. [e]Vibronic satellite bands of the Q band. [f]Q band (for the metal-free **1**, a split Q band is observed).

ning calorimetry (DSC). All samples showed only broad haloes in their diffraction patterns, and exhibited defined, high T_gs in their DSC thermograms (see Table 1). Upon further heating above the T_gs, no crystallization was observed. They are well soluble in organic solvents such as dichloromethane, chloroform, toluene and THF, **4** also in acetone. Amorphous thin films were obtained easily by spin coating onto glass substrates from solution. The morphological stability of **3** was found to be greatly improved over its polymorphic parent compound PcTiO, whose vacuum deposited amorphous film swiftly crystallizes to its α-phase under exposure to ethanol or THF vapors.[5] **1**–**4** do not show any morphological changes from exposure to solvent vapors.

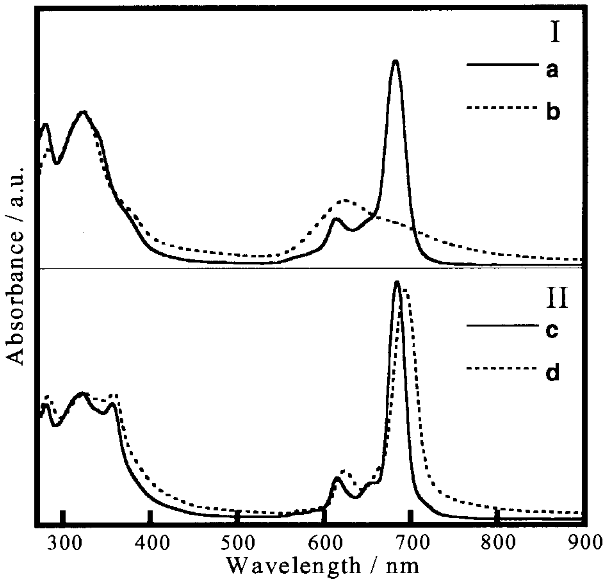


Figure 1. I) a: 2 in CH_2Cl_2; b: spin-coated amorphous film of **2**. II) c: **4** in CH_2Cl_2; d: spin-coated amorphous film of **4**.

All the synthesized compounds show electronic absorption spectra composed of the characteristic Q (red region) and Soret bands (blue region) of a phthalocyanine, the latter overlapping with their quadruple arylamine chromophores' absorption (see also Table 1). Figure 1 shows a comparison of the electronic absorption spectra of **2** and **4** in solution and as amorphous spin coated thin films. While **1**, **2** and **3** show aggregation in the solid state, visible in **2**'s spectrum (see Figure 1, Ib) as a broadening of the Q band into the red region accompanied by a substantial decrease in intensity, **4** is not aggregated and retains the absorption properties of the solution (see Figure 1, IId).

Aggregation is a well-known phenomenon for phthalocyanines whose cores are not kept apart by bulky peripheral or bisaxial substituents, resulting from co-facial π–π interactions between the macrocycle discs.[6] It should be noted that in the case of **1**–**3**, the amorphous state demonstrably prevails over crystallinity despite the aggregation. It can therefore be safely assumed that there is only a short-range ordering into very likely irregularly spaced, short stacks that lack the long-range order required for crystal formation. By contrast, bisaxially bulkily substituted **4** shows very clearly that it is not aggregated in the amorphous solid state, and retains the highly desirable optical properties of the isolated molecule as in solution.

In summary, we have synthesized a new class of well soluble and amorphous phthalocyanines with high T_gs that readily form stable, uniform amorphous thin films by spin coating and are of high interest for their optical and electronic properties. They are expected to find application in organic devices, into which research is currently under way.

M. O. thanks the Japan Society for the Promotion of Science (JSPS) for a post-doctoral grant.

References and Notes

1 Y. Shirota, *J. Mater. Chem.*, **10**, 1 (2000) and references cited therein.

2 a) "Phthalocyanines, Properties and Applications" ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York, (1989–1996), Vol. 1–4. b) M. Hanack and M. Lang, *Adv. Mater.*, **6**(11), 819 (1994) and references cited therein. c) D. Hohnholz, S. Steinbrecher, and M. Hanack, *J. Mol. Struct.*, **231**, 521 (2000) and references cited therein.

3 a) R. D. George and A. W. Snow, *Chem. Mater.*, **6**(10), 1587 (1994). b) N. B. McKeown, *Adv. Mater.*, **11**(1), 67 (1999). c) M. Brewis, G. J. Clarkson, A. M. Holder, and N. B. McKeown, *Chem. Commun.*, **1998**, 969. d) M. Brewis, G. J. Clarkson, V. Goddard, M. Helliwell, A. M. Holder, and N. B. McKeown, *Angew. Chem. Int. Ed.*, **37**(8), 1092 (1998).

4 (2-NDPAO)$_4$PcM Series: **1**: MS (FD, *m/z*): 1751.5, 875.8, 583.9. IR (cm^{-1}): 3053, 3035, 1591, 1499, 1399, 1331, 1269, 1228, 1119, 1072, 949, 748, 696. ^1H NMR ($CDCl_3$): Signals marked br are broad, unresolved bands. δ = 6.97–7.05 (4H, m), 7.18–7.40 (48H, m; $CHCl_3$), 7.49–7.53 (4H, m), 7.55–7.62 (4H, m), 7.69–7.74 (8H, m), 7.81–8.25 (8H, br). Anal. Calcd for $C_{120}H_{78}N_{12}O_4$: C, 82.27; H, 4.49; N, 9.59%. Found: C, 82.24; H, 4.77; N, 9.27%. **2**: MS (FD, *m/z*): 1813.1, 906.6, 604.1. IR (cm^{-1}): 3054, 3036, 1591, 1499, 1467, 1403, 1267, 1229, 1118, 1093, 1052, 951, 848, 815, 747, 695. Anal. Calcd for $C_{120}H_{76}N_{12}O_4Cu$: C, 79.48; H, 4.22; N, 9.27%. Found: C, 79.36; H, 4.68; N, 8.62%. **3**: MS (FD, *m/z*): 1813.4, 906.7, 604.5, 453.7. IR (cm^{-1}): 3053, 3035, 1591, 1499, 1 399, 1331, 1269, 1228, 1119, 1072, 949, 748, 696. ^1H NMR ($CDCl_3$): δ = 6.98–7.10 (4H, m), 7.11–7.45 (44H, m), 7.49–7.57 (4H, m), 7.58–7.67 (4H, m), 7.68–7.88 (12H, br), 8.36–9.15 (8H, br). Anal. Calcd for $C_{120}H_{76}N_{12}O_5Ti$ C, 79.46; H, 4.22; N, 9.27%. Found: C, 79.23; H, 4.52; N, 9.10%. **4**: MS (FD, *m/z*): 2125.0, 1951.0, 1327.1 IR (cm^{-1}): 3054, 3003, 2940, 2861, 1616, 1592, 1499, 1468, 1406, 1353, 1330, 1269, 1231, 1204, 1120, 1081, 1058, 1022, 957, 881, 848, 814, 762, 746, 696, 476. ^1H NMR ($CDCl_3$): δ = –2.07 to –1.96 (6H, m), –1.16 to –1.09 (36H, d), 7.03–7.13 (4H, m), 7.25–7.46 (48H, m), 7.52–7.84 (12H, m), 7.95–8.01 (4H, m), 9.10–9.14 (4H, m), 9.47–9.62 (4H, m). Anal. Calcd for $C_{138}H_{118}N_{12}O_6Si_3$ C, 78.01; H, 5.60; N, 7.91%. Found: C, 78.18; H, 65.95; N, 7.54%.

5 a) T. Tsuzuki, Y. Kuwabara, N. Noma, Y. Shirota, and M. R. Willis, *Jpn. J. Appl. Phys.*, **35**, L447 (1996). b) H. S. Nalwa, T. Saito, A. Kakuta, and T. Iwayanaji, *J. Phys. Chem.*, **97**, 10515 (1993).

6 a) M. J. Stillman and T. Nyokong in "Phthalocyanines, Properties and Applications" ed. by C. C. Leznoff and A. B. P. Lever, VCH, New York, (1986), Vol. 1. b) W. J. Schutte, M. Sluyters-Rehbach, and J. H. Sluyters, *J. Phys. Chem.*, **97**, 6069 (1993). c) M. Cook, *Pure Appl. Chem.*, **71**(11), 2145 (1999).