a Rigaku AFC-5R four-circle automated diffractometer using a rotating anode generator with graphite monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54178$ Å). The crystals were mounted on a glass capillary tube. The reflection intensities for **6** were monitored by three standard reflections at every 2 h and 150 measurements, and the decay of intensities for the crystals was within 2%. Refraction data were corrected for both Lorentz and polarization effects. **1**: $C_{54}H_{56}N_8O_2Cu_2I_2$, pale yellow crystals, monoclinic, space group $P2_1/n$, $a = 13.704(9)$, $b = 8.349(2)$, $c = 23.318(4)$ Å, $\beta = 89.88(3)^\circ$, $V = 2667(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.531\ g\,cm^{-3}$, $R = 0.081$, $R_w = 0.141$ for all 6345 reflections ($I > 2.0\sigma(I)$) and 308 parameters. **2**: $C_{47}H_{42}N_4OBCu$, colorless crystals, monoclinic, space group $P2_1/n$, $a = 11.5365(3)$, $b = 22.5800(5)$, $c = 15.8994(5)$ Å, $\beta = 107.8117(6)^\circ$, $V = 3934.2(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.269\ g\,cm^{-3}$, $R = 0.061$, $R_w = 0.100$ for all 7975 reflections ($I > 2.0\sigma(I)$) and 488 parameters. **6**: $C_{26}H_{22}N_4OCl_6$, colorless crystals, monoclinic, space group $P2_1/c$, $a = 10.743(3)$, $b = 17.820(4)$, $c = 15.673(3)$ Å, $\beta = 105.72(2)^\circ$, $V = 2887(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.424\ g\,cm^{-3}$, $R = 0.085$, $R_w = 0.088$ for all 4287 reflections ($I > 2.0\sigma(I)$) and 335 parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159430–159432, for **1**, **2**, and **6**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[17] Spectral changes observed on oxygenation of **2** and [Cu(bnp)I] as well as an ORTEP view of **6** can be found in the Supporting Information.

[18] P. L. Holland, C. J. Cramer, E. C. Wilkinson, S. Mahapatra, K. R. Rodgers, S. Itoh, M. Taki, S. Fukuzumi, L. Que, Jr., W. B. Tolman, *J. Am. Chem. Soc.* **2000**, *122*, 792.

[19] E. Pidcock, S. DeBeer, H. V. Obias, B. Hedman, K. O. Hodgson, K. D. Karlin, E. I. Solomon, *J. Am. Chem. Soc.* **1999**, *121*, 1870.

[20] [Cu(bbp)I] was revealed to have the same dimeric structure as that of **1** by X-ray analysis (unpublished result), while the structure of [Cu(bnp)I] is not established yet. Therefore, these complexes are tentatively expressed as monomers.

[21] Y. Shimazaki, S. Huth, A. Odani, O. Yamauchi, *Angew. Chem.* **2000**, *112*, 1732; *Angew. Chem. Int. Ed.* **2000**, *39*, 1666.

Immobilization of π-Assembled Metallo-Supramolecular Arrays in Thin Films: From Crystal-Engineered Structures to Processable Materials[**]

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Material and device performance is critically dependent on the spatial arrangement of the functional constituents. The ability to control the short- and long-range correlation of position and orientation of components is crucial for full exploitation of a material's potential and the encoding of new properties.[1] Supramolecular synthetic methodologies enable the systematic design and construction of tailored architectures through a sequence of directed assembly processes.[2] Metallo-units are particularly attractive functional components because of their inherent magneto-,[3] electro-,[4] and/or photochemical[5] properties.

By means of crystal engineering, solid-state multimetal arrays can be constructed by using interactions of metal ions with multitopic ligands[6] or other intermolecular forces to organize metallo-units.[7–9] However, processing a crystalline solid into a device remains a challenge. Moreover, in a single crystal, it is difficult to achieve attractive features such as gradients, often necessary for vectorial functions. Thin films play an important role in applications[10] such as storage, display, and sensing, yet to date there are no generic methodologies for incorporating and ordering discrete cationic metal complexes into thin films.[11] To address this challenge and to attempt to bridge the gap between fundamental supramolecular crystal engineering and layered materials, we investigated whether π-aggregated metallo-arrays can be incorporated into ordered two-dimensional thin films.

A particularly attractive method to assemble thin films is the layer-by-layer (LbL) method, which rests primarily on

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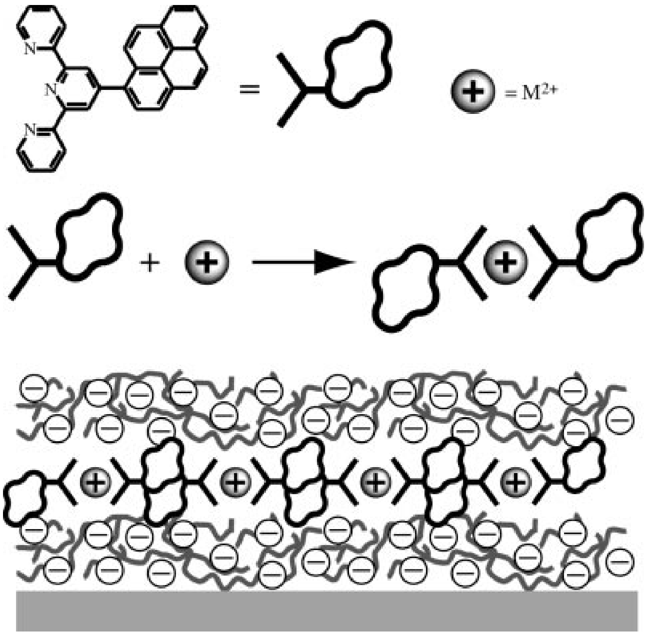
electrostatic interactions between charged species in solution and an oppositely charged surface.[12, 13] The experimental implementation of this technique is straightforward and relies simply on dipping the substrate into solutions containing the species to be deposited. The method permits thickness control on a nanometer scale, can be applied to arbitrary substrates (including nanoparticles), and is readily automated. In addition, layers of different functional components can be systematically placed within the thin film. While this method has been successfully applied to metallo-supramolecular coordination polyelectrolytes,[14] it has never been convincingly demonstrated with discrete metallo-units.[15]

Previously, it was demonstrated that aryl tails can be used to control the aggregation of metallo-units into ordered linear rodlike arrays assembled by π–π interactions.[9] Such arrays have several advantages over conventional coordination polymers: Facile ligand synthesis; reversible assembly, even with inert metal ions; good solubility; and straightforward characterization. Reasoning that π–π interactions might be sufficient to order a structure at an interface, we examined whether these structures can be placed in films by LbL deposition (Scheme 1).



Scheme 1. Immobilization of discrete metallo-units in thin films by combining electrostatic attraction of oppositely charged species with aryl aggregation of metallo-units.

We selected pyrene as the aryl moiety to achieve control over the supramolecular organization. Pyrene has a strong propensity to form face-to-face pyrene–pyrene stacks, which can be detected spectroscopically by their characteristic excimer emission bands, and this suggests that pyrenyl tails might be ideal not only as π-aggregation motifs but also as spectroscopic tags for monitoring stacking and aggregation.[16] Reaction of 4′-(1-pyrenyl)-2,2′:6′,2″-terpyridine (Pyr-tpy) with transition metal (M) dications afforded the $[M(Pyr\text{-}tpy)_2]^{2+}$ complex cations, as anticipated from the coordination chemistry of unsubstituted tpy.[17] Crystallographic analysis of the Fe^{II} complex confirmed the anticipated pyrene–pyrene stacking motif (Figure 1).[18] The structure contains six-coordinate Fe^{II} bis-terpyridyl units linked into a rodlike linear array by pyrene–pyrene π stacking (interplanar separation ca. 3.5 Å; closest C⋯C 3.43 Å).

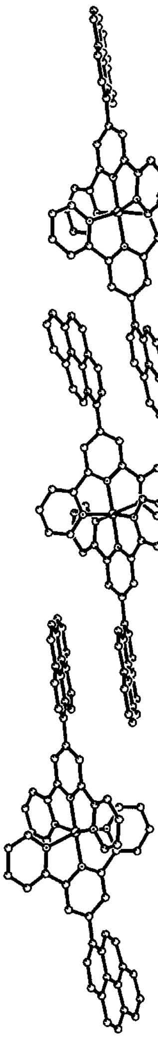


Figure 1. Packing of the cations to give a linear rodlike array in the crystal structure of $[Fe(Pyr\text{-}tpy)_2](ClO_4)_2$.

Using polystyrenesulfonate (PSS) as counterpolyelectrolyte, we observed multilayer formation with $[M(Pyr\text{-}tpy)_2]^{2+}$ complexes (M = Zn, Fe). In contrast, simple bis-terpyridine complex cations $[M(tpy)_2]^{2+}$, which do not bear aryl tails, do not form multilayers under these conditions. While such complexes are adsorbed on PSS surfaces, the layer is generally removed in the following step when the next layer of PSS is deposited. From this it is clear that the aryl tails play a vital role in the deposition of Pyr-tpy complexes at the interface.

The UV/Vis absorption spectra of multilayers of $[Zn(Pyr\text{-}tpy)_2]^{2+}$ are shown in Figure 2a. The presence of the characteristic absorption bands at 420, 334, 290, and 250 nm demonstrate the incorporation of $[Zn(Pyr\text{-}tpy)_2]^{2+}$ in the multilayer film. Compared to the spectrum in methanol solution (inset 1), the bands are somewhat broadened and shifted. The loss of fine structure is associated with packing effects, while the shift is due to the different local polarity in the multilayer.[19] A plot of the absorption maxima as a function of the number of layers confirms linear multilayer buildup, that is, equal amounts of material are deposited at the interface in each deposition step (Figure 2a, inset 2). Spectra recorded after deposition of PSS reveal that $[Zn(Pyr\text{-}tpy)_2]^{2+}$ is partly removed from the surface. Partial desorption during LbL deposition was observed in other cases and was attributed to weakly bound excess material.[20] Layer deposition involves concomitant desorption of $[Zn(Pyr\text{-}tpy)_2]^{2+}$ and deposition of PSS, and therefore quantification of the amount deposited is meaningful only for a {PSS/metallo-unit} layer pair. From the absorbance at 338 nm, the surface coverage is approximately 1.1 metallo-units per square nanometer or 0.9 nm² per metallo-unit.[21] The dimensions of the metallo-unit can be estimated from the crystal structure.[18] The unit is about 2.5 nm long (pyrene to pyrene), and the width of the terpyridine moieties is about 1.1 nm. For surface coverage, the two limiting cases would be for the units to lie flat with their long axis parallel to the substrate or, alternatively, to stand perpendicular. The occupied surface area is about 3.0 nm² per unit if independent (non-π-stacked) units lie flat on the

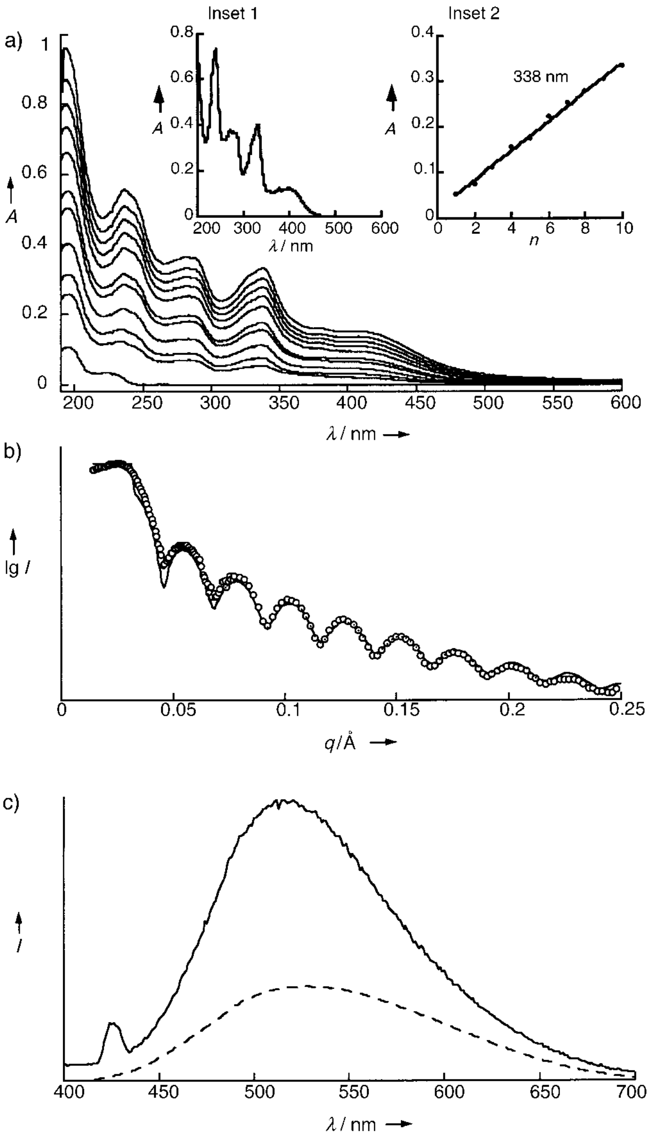


Figure 2. a) UV/Vis absorption spectra of {[Zn(Pyr-tpy)$_2$]$^{2+}$/PSS} multilayers. Inset 1) Spectrum of [Zn(Pyr-tpy)$_2$]$^{2+}$ in methanol. Inset 2) Absorbance at 338 nm as a function of the number of layers. b) X-ray reflectance data (dots) and curve fit (solid line) for a PEI/PSS{[Zn(Pyr-tpy)$_2$]$^{2+}$/PSS}$_{10}$ multilayer on silicon. c) Emission-spectra of a PEI/PSS{[Zn(Pyr-tpy)$_2$]$^{2+}$/PSS}$_{13}$ multilayer on quartz (solid line) and solid [Zn(Pyr-tpy)$_2$](PF$_6$)$_2$ deposited on the quartz plate (intermittent line) (λ_{exc} = 330 nm).[26] A = absorbance, I = intensity, q = scattering vector.

surface, and about 1.2 nm^2 if they stand upright. However, if the units lie flat with the long axis parallel to the substrate and are π-stacked (as in the crystal structure; metal–metal distance ca. 1.7 nm) the area occupied falls to about 2.0 nm^2. From these dimensions, the experimentally determined surface coverage therefore corresponds approximately to one to two molecular layers.

The multilayers are very smooth, as demonstrated by the occurrence of Kiessig interference fringes in the X-ray reflectance spectrum shown in Figure 2b for a {PSS/[Zn(Pyr-tpy)$_2$]}$_{10}$/PSS multilayer. From the fit of the curve, shown as solid line, we determine the surface roughness to be less than 1 nm, and the thickness of a layer pair to be 2.5 nm.[22] The thickness was independently confirmed by optical ellipsometry (data not shown). The thickness suggests that films are composed approximately of molecular layers of [Zn(Pyr-tpy)$_2$]$^{2+}$ and PSS, which is in agreement with the UV/Vis data. This value also precludes orientation of the units perpendicular to the substrate. We therefore propose that the metallo-units lie flat on the surface, which would permit full π aggregation. Experimental confirmation of this is presented below.

Similar results were obtained with Fe^{II} as central metal ion. The structural integrity of the metallo-unit in the multilayer is confirmed by the characteristic metal-to-ligand charge-transfer (MLCT) absorption at at 579 nm. As with Zn^{II} as central metal ion, the absorption data (not shown) confirm linear growth of multilayers. Likewise, these multilayers are very smooth and homogeneous, as indicated by the X-ray reflectance measurements (data not shown).

A solution of [Zn(Pyr-tpy)$_2$]$^{2+}$ in methanol shows a characteristic fluorescence band at 455 nm attributed to the luminescence of the molecular units, as was observed with previously reported zinc terpyridyl complexes.[9] In contrast, upon irradiation of the [Zn(Pyr-tpy)$_2$]$^{2+}$ multilayer film at 330 nm we observe a very broad and structureless emission band centered around 520 nm (Figure 2c). Solid [Zn(Pyr-tpy)$_2$](PF$_6$)$_2$ deposited on quartz shows a very similar emission band. The band is characteristic of excimer or excimerlike emission[23] from the π-stacked pyrene units. This band is also observed in the solid free Pyr-tpy ligand, which also contains stacked pyrene units.[24] The observation of excimer emission in the thin film of the zinc complex is conclusive evidence that the pyrene tails are stacked in the film in the same structural motif as in the solid state. The absence of any detectable 455 nm fluorescence in multilayers of [Zn(Pyr-tpy)$_2$]$^{2+}$ implies that virtually all metallo-units engage in π stacking in each layer (as in the crystal). Multilayers or solid samples of the Fe^{II} complex do not exhibit excimer luminescence due to the MLCT, which lies close in energy to the excimer state and quenches the luminescence. We are currently investigating the application of these metallo-units in other film-forming technologies[25] and extending this LbL approach to a range of other metallo-units and tails.

Experimental Section

The ligand Pyr-tpy and the metal complexes were prepared by procedures analogous to those previously reported for aryl terpyridines.[9] Emission experiments used instrumentation as previously described.[9] Multilayers were prepared and characterized according to a published procedure.[14] Compound **1** was dissolved in water/methanol (1/3). The concentration used for layer-by-layer deposition was 10^{-3} M.

[Zn(Pyr-tpy)$_2$](PF$_6$)$_2$: ^{1}H NMR (CD$_2$Cl$_2$, 300 MHz, 298 K): δ = 8.99 (2H, s, H3'), 8.58 (2H, d, J = 7.6 Hz, H3), 8.54–8.33 (8H, Pyr), 8.21 (3H, m, H4, Pyr), 8.06 (2H, d, J = 5.5 Hz, H6), 7.59 (2H, ddd, J = 7.6, 0.9 Hz, H5); MS (FAB$^+$): m/z: 930 [Zn(Pyr-tpy)$_2$]$^+$.

[Fe(Pyr-tpy)$_2$](ClO$_4$)$_2$: ^{1}H NMR (CD$_3$CN, 300 MHz, 298 K): δ = 9.31 (2H, s, H3'), 8.89 (1H, d, Pyr), 8.66 (2H, d, Pyr), 8.61 (2H, d, J = 8.1 Hz, H3), 8.50–8.41 (5H, Pyr), 8.25 (1H, Pyr), 7.97 (2H, td, J = 7.7, 2.1 Hz, H4), 7.47 (2H, d, J = 5.1 Hz, H6), 7.24 (2H, ddd, J = 7.0, 1.1 Hz, H5); MS (FAB$^+$): m/z: 922 [Fe(Pyr-tpy)$_2$]$^+$, 1021 [Fe(Pyr-tpy)$_2$ClO$_4$]$^+$.

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[1] J. Simon, J. J. André, A. Skoulios, *New J. Chem.* **1986**, *10*, 295–311; J. Simon, F. Tournilhac, J. J. André, *New J. Chem.* **1987**, *11*, 383–399; J. Simon, P. Bassoul, S. Norvez, *New J. Chem.* **1989**, *13*, 13–31.

[2] J.-M. Lehn, *Supramolecular Chemistry—Concepts and Perspectives*, VCH, Weinheim, **1995**; D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1155–1196.

[3] O. Kahn, C. J. Martinez, *Science* **1998**, *279*, 44.

[4] P. L. Boulas, M. Gómez-Kaifer, L. Echegoyen, *Angew. Chem.* **1998**, *110*, 226–258; *Angew. Chem. Int. Ed.* **1998**, *37*, 216–247.

[5] V. Balzani, F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, New York, **1991**.

[6] See for example M. J. Zaworotko, *Chem. Commun.* **2001**, 1–9; R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735–3744.

[7] A. D. Burrows, C. W. Chan, M. M. Chowdhry, J. E. McGrady, D. M. P. Mingos, *Chem. Soc. Rev.* **1995**, *24*, 351–359; M. D. Ward, C. M. White, F. Barigelletti, N. Armaroli, G. Calogero, L. Flamigni, *Coord. Chem. Rev.* **1998**, *171*, 481–488.

[8] L. J. Childs, N. W. Alcock, M. J. Hannon, *Angew. Chem.* **2001**, *40*, 1113–1115; *Angew. Chem. Int. Ed.* **2001**, *40*, 1079–1081; M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 1805–1806.

[9] N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc. Dalton Trans.* **2000**, 1447–1461.

[10] J. D. Swalen, D. L. Allara, J. D. Andrade, E. A. Chandross, S. Garoff, J. Israelachvili, T. J. McCarthy, R. Murray, R. F. Pease, J. F. Rabolt, K. J. Wynne, H. Yu, *Langmuir* **1987**, *3*, 932–950.

[11] For examples of thin films with metal ions, see T. E. Mallouk, J. A. Gavin, *Acc. Chem. Res.* **1998**, *31*, 209–217; M. Maskus, H. D. Abruna, *Acc. Chem. Res.* **1996**, *12*, 4455–4462; Y. Liang, R. H. Schmehl, *J. Chem. Soc. Chem. Commun.* **1995**, 1007–1008; D. G. Kurth, P. Lehmann, M. Schütte, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 5704–5707; A. Hatzor, T. Moav, H. Cohen, S. Matlis, J. Libman, A. Vaskevich, A. Shanzer, I. Rubinstein, *J. Am. Chem. Soc.* **1998**, *120*, 13469–13477.

[12] G. Decher, *Science* **1997**, *277*, 1232.

[13] M. Lahav, R. Gabai, A. N. Shipway, I. Willner, *Chem. Commun.* **1999**, 1937–1938; M. Lahav, V. Heleg-Shabtai, J. Wasserman, E. Katz, I. Willner, H. Durr, Y.-Z. Hu, S. Bossmann, *J. Am. Chem. Soc.* **2000**, *122*, 11480–11487.

[14] M. Schütte, D. G. Kurth, M. R. Linford, H. Cölfen, H. Möhwald, *Angew. Chem.* **1998**, *110*, 3058–3061; *Angew. Chem. Int. Ed.* **1998**, *37*, 2891–2894; D. G. Kurth, C. Schüler, F. Caruso, *Chem. Commun.* **1999**, 1579–1580.

[15] T. Salditt, Q. An, A. Plech, J. Piesl, C. Eschbaumer, C. H. Weidl, U. S. Schubert, *Thin Solid Films* **1999**, *354*, 208–214; U. S. Schubert, C. Eschbaumer, Q. An, T. Salditt, *J. Inclusion Phenom. Macrocyclic Chem.* **1999**, *35*, 35–43.

[16] A range of aryl tails, including the biphenyl tails previously described in ref. [9], facilitate incorporation in films; the discussion herein is restricted to the pyrenyl tails because of their useful spectroscopic tag.

[17] A square-planar Pt^{II} complex of this Pyr-tpy ligand was recently reported: J. F. Michalec, S. A. Bejune, D. R. McMillin, *Inorg. Chem.* **2000**, *39*, 2708–2709.

[18] Crystal data for $C_{62}H_{38}N_6FeCl_2O_8 \cdot 3(CH_3NO_2)$: $M_r = 1304.87$, triclinic, space group $P\bar{1}$, $a = 11.997(10)$, $b = 12.800(10)$, $c = 21.665(10)$ Å, $\alpha = 89.762(10)$, $\beta = 75.457(10)$, $\gamma = 65.724(10)^\circ$, $V = 2916.79(4)$ Å^3, $T = 180(2)$ K, $\lambda = 0.71073$, $Z = 2$, $\rho_{calcd} = 1.486$ Mg m^{-3}, $F(000) = 1344$. $\mu(Mo_{K\alpha}) = 0.429$ mm^{-1}; purple plate, crystal dimensions $0.3 \times 0.2 \times 0.19$ mm; data were collected on a Siemens SMART three-circle system with CCD area detector. The crystal was held at 180(2) K with an Oxford Cryosystem Cryostream Cooler; $\theta_{max} = 29.16^\circ$. A total of 18515 reflections were measured, 13214 of which were unique ($R_{int} = 0.0159$). Absorption correction by Psi scans. Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0383\,P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$. GOF on F^2 was 1.507, $R1 = 0.0537$ (for 10583 reflections with $I > 2\sigma(I)$), $wR2 = 0.2091$. Data/restraints/parameters: 13214/0/823. Largest difference Fourier peak and hole: 1.294 and −0.894 e Å^{-3}. Refinement used SHELXL97 (G. M. Sheldrick, Universität Göttingen, **1997**). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160346. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[19] *Spectroscopy and Relaxation of Molecular Liquids* (Eds.: D. Steele, J. Yarwood), Elsevier, Amsterdam, **1991**.

[20] D. G. Kurth, D. Volkmer, M. Ruttorf, B. Richter, M. J. Koop, A. Müller, *Chem. Mater.* **2000**, *12*, 2829–2831.

[21] The surface coverage Γ was calculated according to $\Gamma = 3/4(A_\lambda N)/\varepsilon_\lambda$, where ε_λ is the molar extinction coefficient [$\text{M}^{-1}\,\text{cm}^{-1}$] corrected for in-plane anisotropy, N is Avogadro's constant, and A_λ is the absorbance. The calculation assumes that ε is approximately the same in the thin film as in solution.

[22] D. G. Kurth, R. E. Osterhout, *Langmuir* **1999**, *15*, 4842–4846.

[23] F. M. Winnik, *Chem. Rev.* **1993**, *93*, 587–614.

[24] The π–π stacking in the free ligand was confirmed by crystallographic analysis, which will be reported in forthcoming publications.

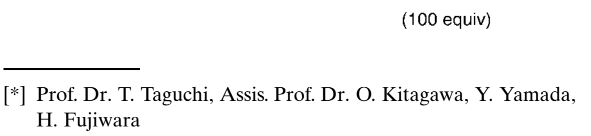
[25] While the multilayers are stable towards solvents (water, alcohol, benzene, etc.), exposure to ethylenediaminetetraacetic acid (EDTA) disassembles the films (pH 11, room temperature). Such externally induced disassembly offers novel opportunities to fabricate membranes for controlled-release applications (see for instance G. B. Sukhorukov, E. Donath, S. Moya, A. S. Susha, A. Voigt, J. Hartmann, H. Möhwald, *J. Microencapsulation* **2000**, *17*, 177–185).

[26] The intensity is not in scale for the two spectra, which are not corrected for photomultiplier tube response.

Iodoaziridine Derivatives as Novel Azahomoallyl Radical Precursors for [3+2] Cycloaddition Reactions with Alkenes

Osamu Kitagawa, Yoichiro Yamada, Hiroki Fujiwara, and Takeo Taguchi*

The [3+2] cycloaddition of a homoallyl radical with an alkene is a powerful method for the one-step synthesis of a cyclopentanoid skeleton.[1] If such a cycloaddition could be achieved with an azahomoallyl (allylaminyl) radical, it would provide a new and useful methodology for the preparation of pyrrolidine derivatives from simple substrates. As far as we know, only one example of the generation of an azahomoallyl radical and its reaction with an alkene has been reported, by Newcomb et al. [Eq. (1)].[2] This method using *N*-allyl *N*-hydroxypyridine-2-thione carbamates as an azahomoallyl



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