Staircase-form assembly with 5,15-bis(imidazol-4-yl)porphinatogallium steps

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Large supramolecular assemblies of 5,15-bis(imidazol-4-yl)porphinatogallium **2Ga** have been synthesized by hexacoordination of two imidazolyl groups to Ga(III) in a staircase arrangement of porphyrin planes as each "step". The structure of the supramolecular assembly was characterized by UV, X-ray diffraction, and AFM. The conductivity of **2Ga** films was enhanced 8 times by photoirradiation.

Introduction

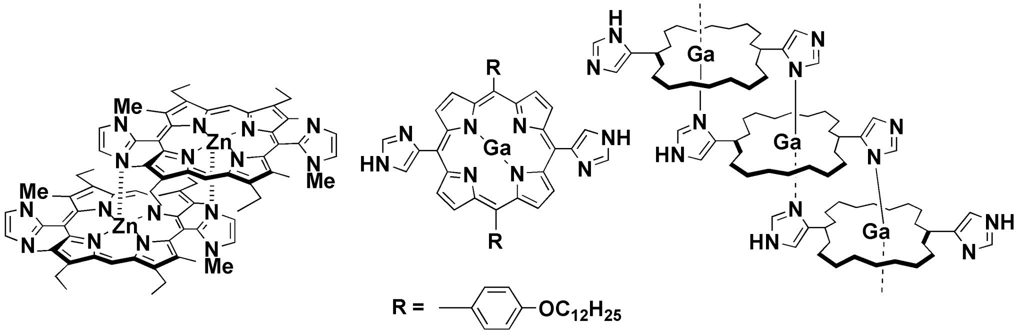
Synthesis of molecular wires and switches is the first target to opening the world of molecular electronics.[1] Many attempts to construct supramolecular wires for efficient transport of electrons/holes and excitons have been reported by the use of non-covalent[2–4] linkages of porphyrins. Most of these systems were constructed in the solid state or in highly concentrated solution such as under NMR conditions (mmol dm^{-3}). Only a few systems[3a–d,4] have been reported for the preparation of supramolecular wires in solution by the use of the large binding constants ($K > 10^8$ dm^3 mol^{-1}). In the mid-1990s, we succeeded in preparing the special pair model[3a] by slipped cofacial coordination of *meso*-substituted bis(*N*-methylimidazol-2-yl)porphinatozinc **1Zn**.[3a] The binding constant of **1Zn** in $CHCl_3$ is more than 10^9 dm^3 mol^{-1}. This large binding constant is a result not only of complementary imidazolyl coordination to the zinc ion, but also of π–π stacking interactions between two porphyrin rings. Therefore, imidazolylporphyrin zinc complexes may be one of the most ideal molecular units for constructing supramolecular wires. We have recently succeeded in constructing a giant supramolecular porphyrin array (~800 porphyrin units based on GPC) by extending this strategy.[3c] We report here the preparation of a novel coordination polymer of a bis(imidazol-4-yl)porphyrin gallium complex by the use of hexacoordinating gallium(III) as the central metal ion (Scheme 1).

Results and discussion

Thec choice of the gallium(III) ion is based on the following two reasons. Firstly, hexacoordination of Ga ions is well established in coordination chemistry and actually Ga porphyrin forms a complex with two nitrogen ligands.[5] Moreover, coordination of imidazolate anion to gallium(III) ion will be stronger than that of neutral imidazolyl nitrogen to gallium(III) ion. Secondly, the d^{10} electronic configuration is free from excitation energy quenching and appropriate for constructing photocontrollable supramolecular switches.[6] Hexacoordinated Co porphyrin complexes[4] are certainly one of the candidates for supramolecular wires. However Co porphyrins are not suitable for a photo-controllable wire, because of the fast radiationless decay of the excitation energy.[6]

Synthesis of Ga complex 2Ga

Bis(imidazol-4-yl)porphinatogallium complex **2Ga** was prepared by mixing the free base **2** with excess $GaCl_3$ in $CHCl_3$–MeOH followed by washing the $CHCl_3$ layer with saturated aqueous sodium bicarbonate.[3c] The insertion of Ga(III) ion was confirmed by MALDI-TOF mass, UV and fluorescence spectra. Significant line broadening in the ^1H NMR spectrum of **2Ga** precluded unfortunately the use of NMR spectroscopy. Fig. 1 shows the MALDI-TOF mass spectrum of bis(imidazolyl)porphinatogallium complex **2Ga** (using



1Zn **2Ga** staircase type assembly

Scheme 1

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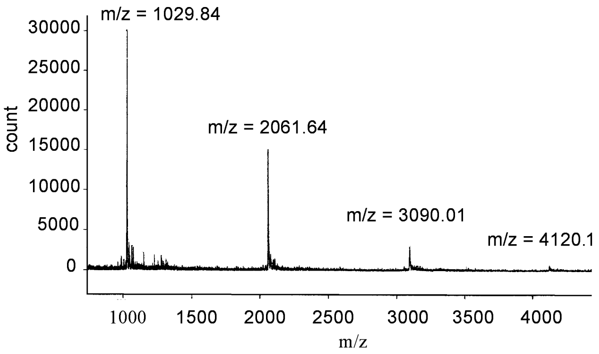


Fig. 1 MALDI-TOF mass spectrum of bis(imidazolyl)porphinatogallium complex, **2Ga**.

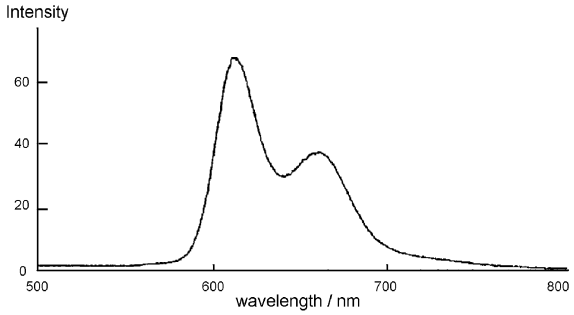


Fig. 2 Fluorescence spectrum of **2Ga** in $CHCl_3$ at 6 μmol dm^{-3}. λ_{EX} = 438 nm.

dithranol as a matrix, M_w = 1029.84). As expected, the peak with the highest intensity was observed at 1030 mass units. In addition to this signal, there were observed three additional peaks at 2061.64, 3090.01, 4120.1 mass units, corresponding to dimers, trimers, and tetramers of **2Ga**, respectively. Fluorescence peak intensities of **2Ga** were relatively strong, as expected (Fig. 2).[6]

Split Soret band of porphyrin arrays

The bis(imidazolyl)porphinatozinc complex, **2Zn**, was also prepared as a reference compound from the corresponding free base porphyrin **2** and zinc acetate. The structure was confirmed by ^{1}H-NMR, MALDI-TOF mass, and UV-Vis spectra. The ^{1}H-NMR spectrum of **2Zn** was broad in $CDCl_3$ due to the formation of hydrogen-bond networks. In a solution containing 2.2 mol dm^{-3} d_4-methanol, the peaks of the ^{1}H-NMR spectrum of **2Zn** were sharpened and were identified as the zinc dimer complex by comparison with the spectrum of *N*-methylimidazolylporphinatozinc.[3a] Since **2Zn** dimer has imidazolyl N–H groups, they can interact with each other through hydrogen-bonds in $CDCl_3$ as shown in Scheme 2a.

Like other imidazolylporphinatozinc complexes, **2Zn** has two split Soret bands at 418 and 430 nm in the UV-Vis spectrum in $CHCl_3$ as shown in Fig. 3. These splittings are caused by the exciton coupling of the corresponding B transitions of porphyrins in a slipped cofacial arrangement as shown in Scheme 3.[3,7] There are two in-plane transition moments, M_y and M_z, in monomeric porphyrin. In the case of **2Zn**, the Soret band is split into two peaks: blue shifted 418 nm for the M_z component of face to face orientation and red shifted 430 nm for the M_y component with head to tail excitons. The hydrogen-bonds in **2Zn** do not seem to have an effect on the split, since free base porphyrin gave only broadening of the peak.[3e] The supramolecular array **2Ga** showed very large split Soret bands compared to Zn complex **2Zn** (Fig. 3). In the case of **2Ga**, the Soret band was split into two peaks: 394 nm and 438 nm as more blue shifted M_z and more red shifted M_y components, respectively as shown in Scheme 3. The splitting energy ΔE of **2Ga** (2550 cm^{-1}) is far greater than that of **2Zn** (670 cm^{-1}). Since the splitting energies of Soret bands depend on the number of interacting porphyrins,[8] supramolecular array **2Ga** must have a larger degree of polymerization than **2Zn**.

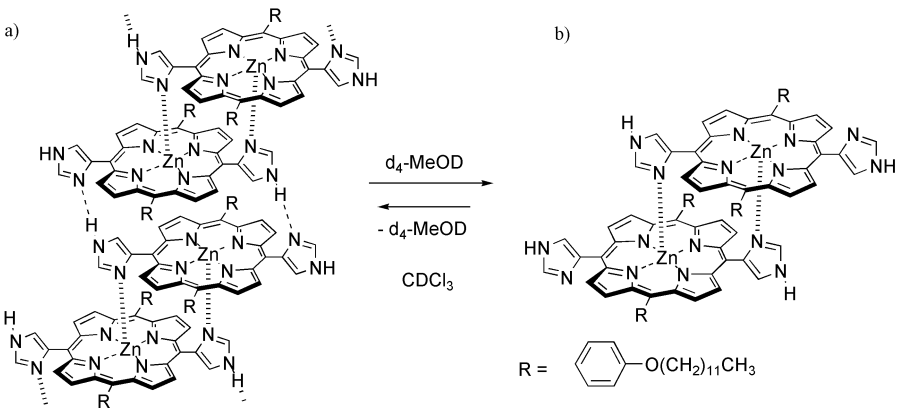
In spite of the above estimation, we could not determine the average molecular weight of supramolecular array **2Ga** by GPC due to the serious adsorption. Low solubility of **2Ga** in $CHCl_3$ also prevented us from determining the average molecular weight of **2Ga** by VPO or DLS measurement.

Molecular modeling

Supramolecular array **2Ga** was constructed using a SGI program Cerius2. Geometry optimization was carried out using the universal 1.02 force field. The geometry obtained for supramolecular array **2Ga** by molecular mechanics calculations (Fig. 4) shows a porphyrin plane like staircase steps.[9] The calculated distance between the porphyrin planes is 0.35 nm. The Ga–Ga distance is 0.6 nm, and the height (Im–Ga–Im) and the width (ω-CH_3–ω-CH_3) of **2Ga** are 1.4 and 4.8 nm, respectively.

X-Ray diffraction study

The size of supramolecular array **2Ga** was also confirmed by X-ray diffraction studies in the solid state.[10] As shown in Fig. 5, clear diffractions were observed at around 31.3° and 45.4° (after 2θ–I conversion). Two peaks appearing close together may indicate the presence of two types of Ga–ligand coordination bonds with similar structures. The lattice constant d = 0.57–0.6 nm was obtained by using Bragg's equation



Scheme 2 Hydrogen-bond network through imidazolyl groups in **2Zn** supramolecular assembly in $CDCl_3$ was cleaved by d_4-MeOD.

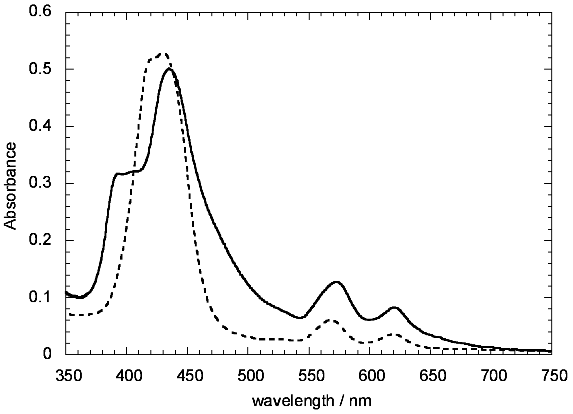


Fig. 3 UV-Vis spectra of bisimidazolylporphyrin complexes in $CHCl_3$. Solid line: **2Ga** (30 µmol dm^{-3}), dotted line: **2Zn** (5 µmol dm^{-3}).

(1).[10] Using the full-width at half-maximum (fwhm) of the Bragg peak, 2.4×10^{-3}–3.1×10^{-3} radians in the X-ray data and the Debye–Scherrer equation (2),[10] the size of supramolecular assembly **2Ga** in the solid state was estimated as 23–28 nm. The evaluated aggregation number of **2Ga** was 66–80 by the use of 0.35 nm as the porphyrin plane–plane distance. Such a diffraction pattern pattern was not observed in the corresponding free base **2**. Coordination of Ga(III) to imidazolyl groups is assumed to be essential to form the staircase-type supramolecular array **2Ga**.

AFM imaging

Fig. 6 displays a tapping mode AFM image of the sample prepared from a solution of **2Ga** in $CHCl_3$ (*ca.* 5 µmol dm^{-3}, 1 µL) on a fresh HOPG substrate surface. Some long plates (150 × 50 nm) were observed on the substrate along with shorter plates (50 × 60 nm). The image of the HOPG substrate prior to the sample application was featureless. The average height of **2Ga** in the topographic AFM image shown in Fig. 6b was 1.8–2.2 nm, which was a little higher than 1.4 nm and shorter than 4.8 nm, the calculated height and width of **2Ga** as shown in Scheme 4. Based on this result, the monomers in the supramolecular assembly **2Ga** possibly spread their alkyl chains in the horizontal direction.

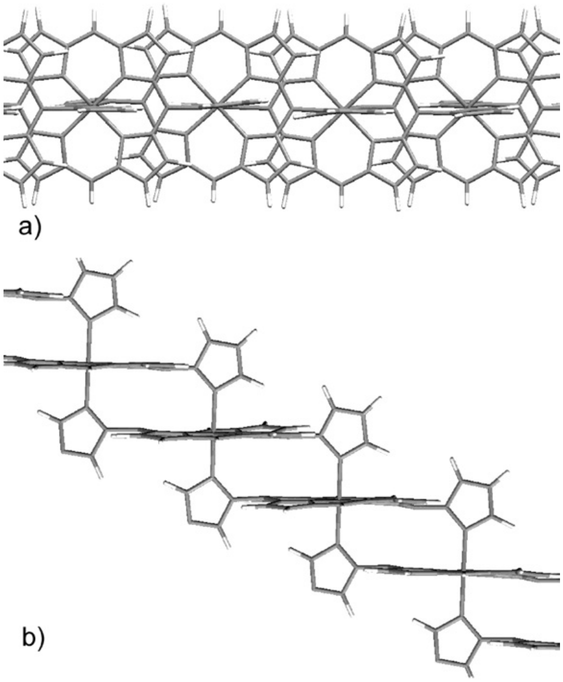
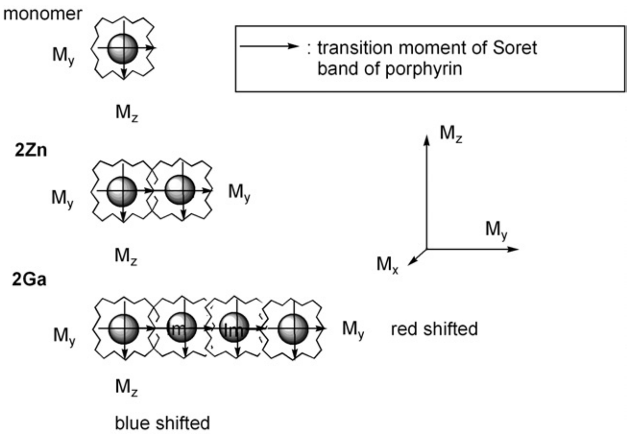


Fig. 4 Minimum energy structure of **2Ga** calculated by Cerius2 with universal force field. Side chains were omitted for the sake of clarity. a) Top view and b) side view with a stick model.

Photo-induced current measurement

The current–voltage characteristics of the **2Ga** supramolecular assembly were measured between gold micro-gap electrodes (gap = *ca.* 100 µm) with/without light irradiation ($\lambda = 532$ nm, a continuous wave YAG laser, 160 mW cm^{-2}). A schematic representation of cells for the measurement of conductivity is shown in Scheme 5. After the sample was dried completely, the currents between the electrodes were measured as shown in Fig. 7. Rough estimates of specific resistances of **2Ga** multilayered films in the dark and under continuous light irradiation are about 1.5×10^6 and 1.8×10^5 Ω m, respectively, assuming that the 100 µm gap and 25 nm depth of the cell were filled with **2Ga**. The current level is still low mainly because of the presence of boundaries between assemblies. Even so, the conductivity between the gap electrodes was increased by 800% upon light irradiation. This large enhancement of the conductivity is particularly noteworthy. The photocurrent of **2Ga** did not change during the measurements with continuous light irradiation for 5 min. The light irradiation may facilitate electron/hole transfers in the **2Ga** array.



Scheme 3 Exciton coupling of bisimidazolylporphyrins **2Zn** or **2Ga** in a slipped cofacial arrangement.

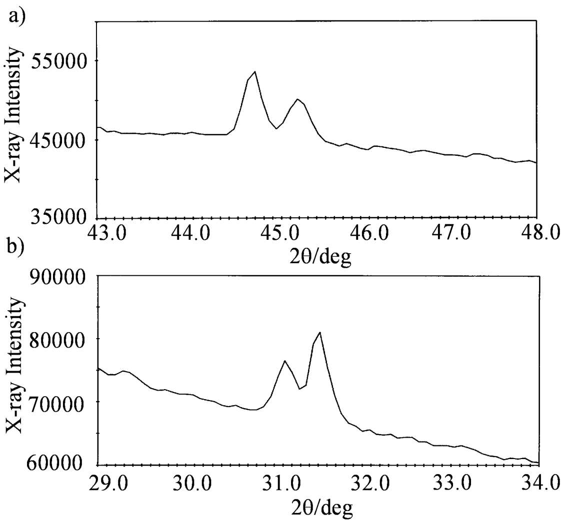


Fig. 5 X-Ray diffraction patterns of **2Ga** self-assembled array. a) Large θ region, b) small θ region.

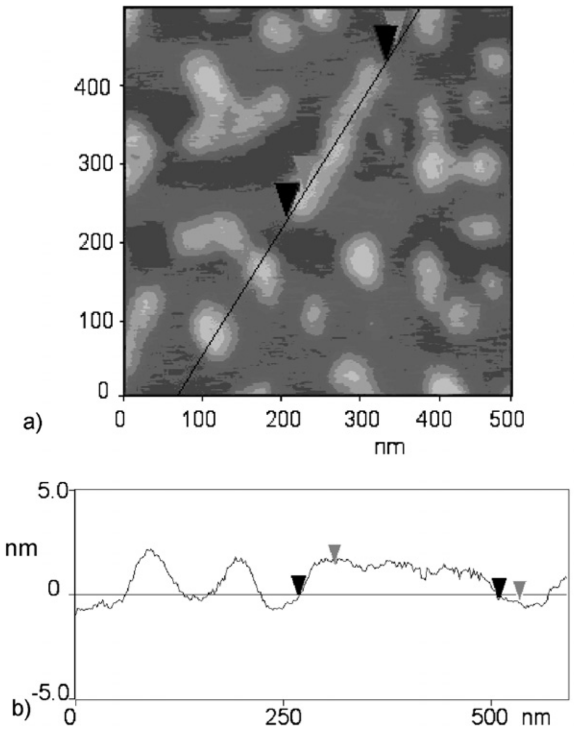


Fig. 6 Topographic image of **2Ga** acquired by AFM on a HOPG substrate. a) Top view, b) section along the line.

Concluding remarks

We have synthesized supramolecular assemblies of 5,15-bis-(imidazol-4-yl)porphinatogallium **2Ga** by axial coordination of two imidazolyl groups to Ga(III) in a staircase arrangement. These results indicate that **2Ga** transports electrons under light irradiation as a photo-supramolecular wire. The calculated distance between adjacent porphyrin planes of the staircase is 0.35 nm, which is similar to the distance (0.34 nm) between adjacent base pairs in B-form of DNA[11] and the distance (0.39 nm) between adjacent porphyrins in discotic liquid crystalline porphyrins.[12a] In these discotic liquid crystalline porphyrins, similar enhancement (*ca.* 5 times) of the conductivity with light irradiation has been observed.[12b] These materials have been studied intensively for new electronic and optoelectronic applications. We believe that the imidazolylporphyrin arrays are one of the suitable candidates for constructing supramolecular light switches or wires.

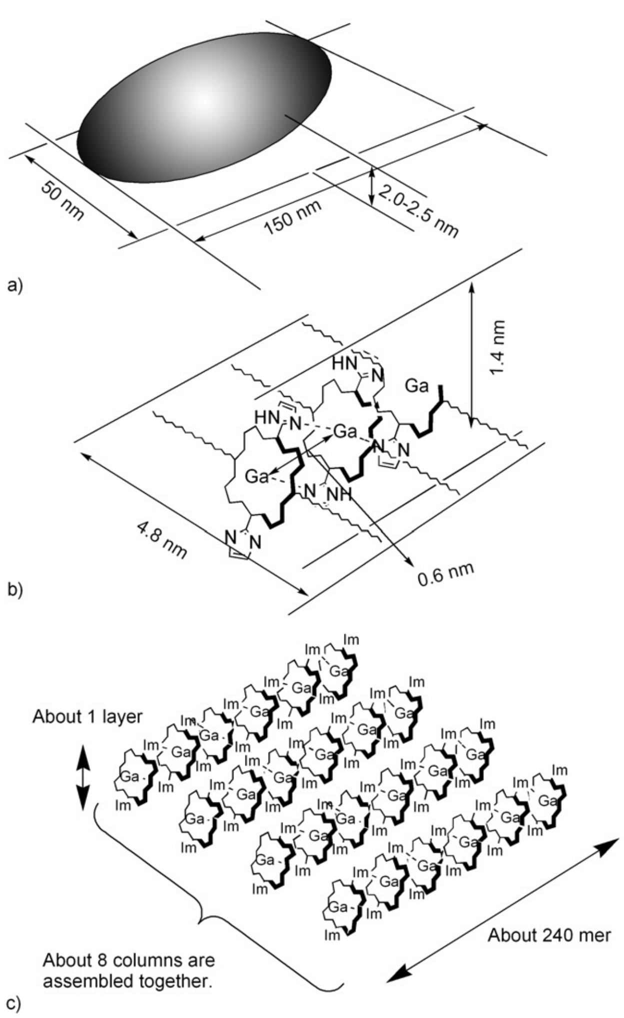
Experimental

Preparation of porphyrin Ga complex, 2Ga

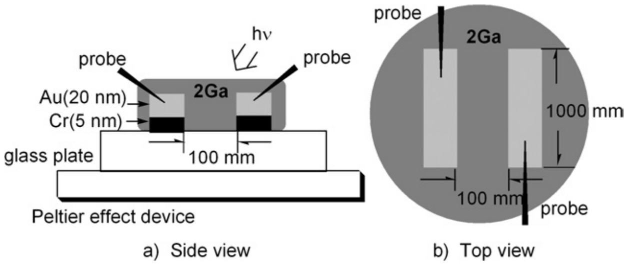
Into a solution of 6.5 mg (6.75 μmol) of free base porphyrin **2** dissolved in 5 mL of $CHCl_3$, 118 mg (675 μmol) of gallium chloride dissolved in 2 mL of ethanol was added. The solution was refluxed for 3 h under Ar. After removal of the solvents, the residue was dissolved in 20 mL of $CHCl_3$ and washed with saturated aqueous sodium bicarbonate solution. The $CHCl_3$ layer was concentrated to dryness. The product was purified by silica gel ($CHCl_3$:CH_3OH 5:1 v/v) chromatography to give dark green crystals **2Ga** (5 mg, 4.86 μmol, yield 72%). UV-Vis ($CHCl_3$) λ_{max}/nm: 394, 438, 566, 623.5. Fluorescence ($CHCl_3$, $\lambda_{EX} = 438$ nm) λ_{EM}/nm: 613, 661. MALDI-TOF mass (dithranol): $m/z = 1029.84$ (calc. M^+: 1029.50 for $C_{62}H_{72}{}^{69}GaN_8O_2)^+$.

Preparation of porphyrin Zn complex, 2Zn

Into a solution of 5 mg (5.2 μmol) of free base porphyrin **2**[3c] dissolved in 6 mL of $CHCl_3$, 95 mg (520 μmol) of zinc acetate dissolved in 5 mL of methanol was added. The solution was refluxed for 1.5 h. After removal of the solvents, the residue was dissolved in 30 mL of $CHCl_3$ and washed with distilled water. The $CHCl_3$ layer was concentrated to dryness. The product was purified by silica gel ($CHCl_3$:CH_3OH 5:1 v/v) chromatography to give dark red crystals **2Zn** (4.2 mg, 4.1 μmol, yield 79%). ^1H NMR (400 MHz, $CDCl_3$ 0.5 ml, CD_3OD 80 μl) δ: 9.04 (4 H, brs, pyrroleβH), 8.95 (4 H, brs, pyrroleβH), 8.51 (4 H, brs, phenoxy), 8.22 (4 H, brs, pyrroleβH), 7.88 (4 H, brs, phenoxy), 7.60 (2 H, s, imidazole), 7.45 (2 H, s, imidazole), 7.40 (4 H, brs, phenoxy), 7.19 (4 H, brs, phenoxy), 5.82 (4 H, brs, pyrroleβH), 4.30 (8 H, brs, OCH_2), 2.00 (8 H, m, $–CH_2–$), 1.65–1.16 (72 H, m, $–(CH_2)_9–$), 1.00 (12H, m, $–CH_3$), UV-Vis ($CHCl_3$) λ_{max}/nm: 418, 431, 568, 619. Fluorescence ($CHCl_3$, $\lambda_{EX} = 431$ nm) λ_{EM}/nm: 626. MALDI-TOF mass



Scheme 4 Schematic illustration of **2Ga** assembly. a) Typical size of **2Ga** observed in AFM, b) unit size calculated by Cerius2, c) estimation of the assembly.



Scheme 5 Dimensions of gold electrodes for photocurrent measurement and **2Ga** film.

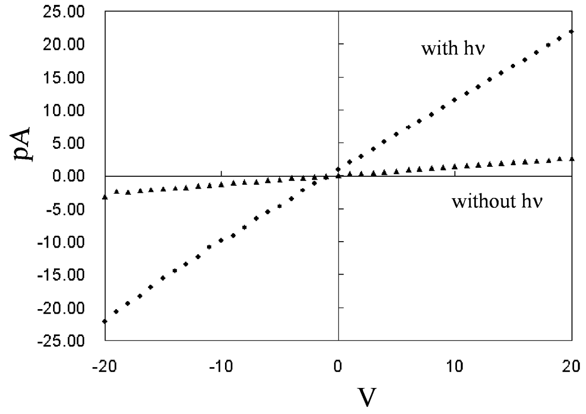


Fig. 7 Photo-induced enhancement of conductivity of **2Ga** with and without light irradiation ($\lambda = 532$ nm).

(dithranol): $m/z = 1025.38$ (M + H) (calc.: 1024.51 for $C_{62}H_{72}N_8O_2{}^{64}Zn$).

X-Ray diffraction

The $CHCl_3$ suspension of the **2Ga** complex (*ca.* 1 mmol dm^{-3}, 0.1 mL) was placed in a quartz capillary tube and evaporated and dried in vacuum. The resultant solid was used directly for the measurements. X-Ray diffraction data were obtained by using a Rigaku R-AXIS IV (Cu K$_\alpha$ radiation: $\lambda = 1.542$ Å). The distance between the CCD camera and the sample was 71 mm. Lattice constant d was calculated by using Bragg's equation,

$$n\lambda = 2d\sin\theta \qquad (1)$$

n being an integer. The Debye–Scherrer equation (2) allowed the estimation of L by introducing the coherence length in relation to $\Delta(2\theta)$ in radians, the fwhm of the Bragg peak, and K, a constant, commonly assigned a value of 0.9.

$$L = \frac{\lambda K}{\cos\theta\Delta(2\theta)} \qquad (2)$$

Conductivity measurements

Micro-gap gold electrodes were prepared by the usual masking-lithographic technique. Glass plates were thermally deposited with chromium (50 Å) and gold (200 Å) at an evaporation rate of approximately 2–3 Å per second. The dimensions of the cell are shown in Scheme 5. The cast film of **2Ga** was obtained by casting a $CHCl_3$ (*ca.* 0.1 mmol dm^{-3}, 1 μL) suspension on the gold electrodes. The **2Ga** film covered the electrodes completely. After the sample was dried under vacuum (0.1 Torr) at room temperature for 3 h, the dark current between the electrodes was measured. The conductivity of the **2Ga** film was measured at 25 °C by a Manual Prober Model705B, Micronics, Japan and a Semiconductor Parameter Analyzer 4156C, Agilent Technologies. The temperature of the sample was controlled at 25 °C by a Peltier effect device. The photocurrent of the **2Ga** film was measured under irradiation with a CW YAG laser (532 nm, 160 mW cm^{-2}). One scan from −20 V to 20 V took about 90 seconds. Three scans were recorded sucessively.

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