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Synthesis of μ-oxo-bridged hetero-metal phthalocyanine dimer analogues and application for charge generating material in photoreceptor

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Abstract

It was found that the concentrated sulfuric acid treatment of an equimolar mixture of a halo-metal phthalocyanine and an oxo-metal phthalocyanine followed by treating in a basic solution gives selectively μ-oxo-bridged hetero-metal phthalocyanine dimer in fairly good yield. This methodology can also serve μ-oxo-bridged hetero-metal phthalocyanine and naphthalocyanine mixed dimers. A specific polymorph of one of the above analogues showed good photoreceptor properties.

Keywords: μ-Oxo-bridged hetero-metal phthalocyanine dimer; μ-Oxo-bridged hetero-metal phthalocyanine and naphthalocyanine mixed dimers; OPC; CGM; Photoreceptor

1. Introduction

In our on going research on μ-oxo-bridged phthalocyanine dimers chemistry [1], we have already reported that the specific polymorphs of this type of phthalocyanine dimers, especially μ-oxo aluminum phthalocyanine dimer and μ-oxo gallium phthalocyanine dimer, have intriguing characteristics for a charge generating material (CGM) of an organic photoconductor (OPC). In order to obtain the variety of the properties as a CGM, we have also studied the synthesis and the properties of (μ-oxo-bridged aluminum phthalocyaninato) gallium phthalocyanine dimer [2]. In this study, described as the general art for phthalocyanine chemistry elsewhere [3], the μ-oxo-bridged hetero-metal phthalocyanine dimer was synthesized by dehydration reaction between hydroxy aluminum phthalocyanine and hydroxy gallium phthalocyanine. However, the homo-metal phthalocyanine dimers, i.e. μ-oxo aluminum phthalocyanine dimer and μ-oxo gallium phthalocyanine dimer, were simultaneously produced as side-products.

2. Results and discussion

2.1. Synthesis

As often happens, the investigation was originally motivated by simple curiosity. We wondered about properties of “μ-oxo-bridged metals phthalocyanine trimer” as a CGM, i.e. bis (μ-oxo gallium phthalocyaninato) titanium phthalocyanine trimer because it is well-known that the individual metal phthalocyanine has a good charge generating property for an OPC devise. Thus, an experiment was carried out to make this type of compound by the reaction of 2 M chlorogallium phthalocyanine and 1 M titanyl phthalocyanine,

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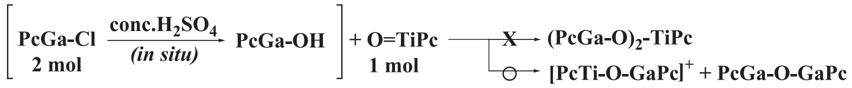


Scheme 1. The proposal reaction scheme to access bis-(μ-oxo-gallium phthalocyaninato) titanium phthalocyanine trimer.

followed by well-known technique of titanyl phthalocyanine with an α,β-dihydroxy compound to afford axial-substituted titanium phthalocyanine derivatives [4]; however, it was found that this reaction did not give the target trimer but the titled μ-oxo-bridged hetero-metal phthalocyanine dimer and the corresponding μ-oxo-bridged homo-metal phthalocyanine dimer by means of MALDI Time-of-Flight Mass-Spectrometry (TOF-MS) (Scheme 1).

The sample for this analysis was prepared as follows: 0.5 mg of the reaction product was dispersed in 10 μl of α-cyano-4-hydroxy cinnamic acid (CHCA) solution, prepared by dissolving 10 mg of CHCA in 1 ml of acetonitrile/water = 1/1 solution. One microlitre of this sample was applied for MALDI-TOFMS with Voyager DE, manufactured by Applied Biosystem Co. Ltd.

The above axial substitution reaction, which we had expected, should have occurred on the same face of a titanium phthalocyanine arising too severe steric hindrance to give the proposal phthalocyanine trimer.

Thus, as shown in Scheme 2, it was carried out to confirm the generality and the selectivity of the equimolar reaction of chloro-metal(1) phthalocyanine and oxo-metal(2) phthalocyanine, affording (μ-oxo-metal(1) phthalocyaninato) metal(2) phthalocyanine, i.e. μ-oxo hetero-metal phthalocyanine dimer, by means of TOF-MS. The reaction results are summarized in Table 1 and the TOF-MS spectrum of the product in entry 1 is shown in Fig. 1.

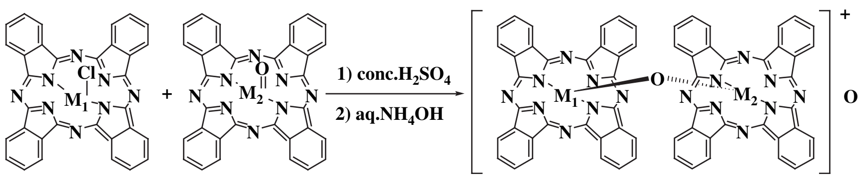
Typical procedure for the synthesis of μ-oxo hetero-metal phthalocyanine dimer is as follows. The mixture of the equimolar amount of chloro-gallium phthalocyanine and titanyl phthalocyanine was dissolved in concentrated sulfuric acid under an ice/methanol bath, stirred for 2 h, and then poured slowly onto large amount of ice over vigorous stirring for 2 h and stand still. The filtrated cake was washed with water until the filtrate shows neutral pH, then subjected to be dispersed again in aqueous ammonium solution for several hours, and filtered, washed with water completely, then dried in an oven under 70 °C.

In order to get a direct evidence to assign the product, we tried to make soluble analogues, bearing peripheral substituents on phthalocyanine rings as shown in Table 1. In this case, the products could be purified through column chromatography packed with neutral aluminum oxide, eluting with THF/chloroform = 1/1 (in the case of entry 7, Rf = 0.8). The experimental entries 6 and 7 gave the corresponding results in the TOF-MS analyses, i.e. entry 6 giving molecular peak at $M^+/e = 1383.9$ and entry 7 giving at $M^+/e = 1607.5$, and the spectrum of the product in entry 7 is shown in Fig. 2.

The analytical data of the product in entry 7 is followed as one of the representative example for this type of product. Yield after column chromatography: 79.4%, ^{1}H NMR (δ 300.4 MHz, $CDCl_3$/ppm) 1.80–1.89 (m, 72H, *t*-Butyl), 8.12–8.30 (m, 8H, aromatic), 8.75–9.41 (m, 16H, aromatic); ^{13}C NMR (δ 75.45 MHz, $CDCl_3$/ppm) 30.5–31.1, 119.0–120.1, 128.8–133.3, 134.1–134.8, 136.2–137.3, 150.1–151.9, 154.2–154.8; IR (ν KBr/cm^{-1}), 3444 (ν_{O-H}), 2958–2866 (ν_{C-H}), 1614 (ν_{C-C}), 1483 (ν_{C-C}), 1081, 764, 752 (ν_{C-H}), 630 ($\nu_{Ti-O-Ga}$: undefined). Anal. calcd. for $C_{96}H_{97}N_{16}O_2GaTi$: C, 70.98; H, 6.02; N, 13.80; Ga, 4.29; Ti, 2.95. Found: C, 70.53; H, 6.03; N, 13.90; Ga, 4.24; Ti, 2.99.

One of the plausible mechanisms could be proposed for the present selective synthesis of μ-oxo-bridged hetero-metal phthalocyanine dimer in Scheme 3.

We have also performed the equimolar reaction of chloro-metal(1) phthalocyanine (Cl–M(1)Pc) or naphthalocyanine (Nc) with oxo-metal(2) phthalocyanine (O=M(2)Pc) or naphthalocyanine to afford (μ-oxo-metal(1) phthalocyaninato or naphthalocyaninato) metal(2) phthalocyanine or naphthalocyanine, i.e. μ-oxo-bridged hetero-metal Pc and Nc mixed dimer. The results are summarized in Table 2 and the TOF-MS spectrum of the product in entry 2 is shown in Fig. 3 and Scheme 4.



Scheme 2. The general reaction scheme of a halo-metal phthalocyanine and an oxo-metal phthalocyanine to afford μ-oxo-bridged hetero-metal phthalocyanine dimmer.

Table 1
The TOF-MS results of various μ-oxo hetero-metal phthalocyanine dimer

Entry	X–MPc	O=MPc	Yield (%)	Calculated $[M-OH]^+/e$	Observed major peak
1	Cl–GaPc	O=TiPc	97.9	1158.64	1159.4
2	Cl–GaPc	O=VPc	90.4	1161.71	1162.7
3	Cl–GaPc	O=MoPc	83.1	1206.71	1205.1
4	Cl–AlPc	O=TiPc	86.6	1115.89	1115.8
5	Cl–AlPc	O=VPc	91.5	1118.97	1118.7
6	Cl–GaPc	O=TiPc(*t*-Bu)$_4$	71.3	1383.06	1383.9
7	Cl–GaPc(*t*-Bu)$_4$	O=TiPc(*t*-Bu)$_4$	79.4[a]	1607.49	1607.5

The above shown phthalocyanine derivatives were synthesized by the common methods in any article [9]. Pc: phthalocyanine.

[a] After column chromatography.

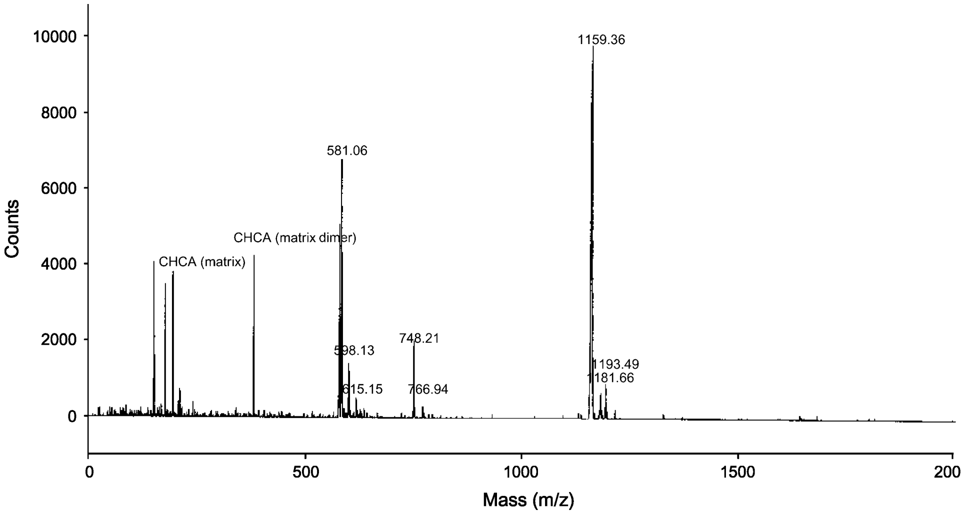


Fig. 1. TOF-MS spectrum of the product, carried out with equimolar Cl–GaPc and O=TiPc under the above mentioned conditions $[PcGa-O-TiPc]^+ = 1159.36$ (entry 1 in Table 1).

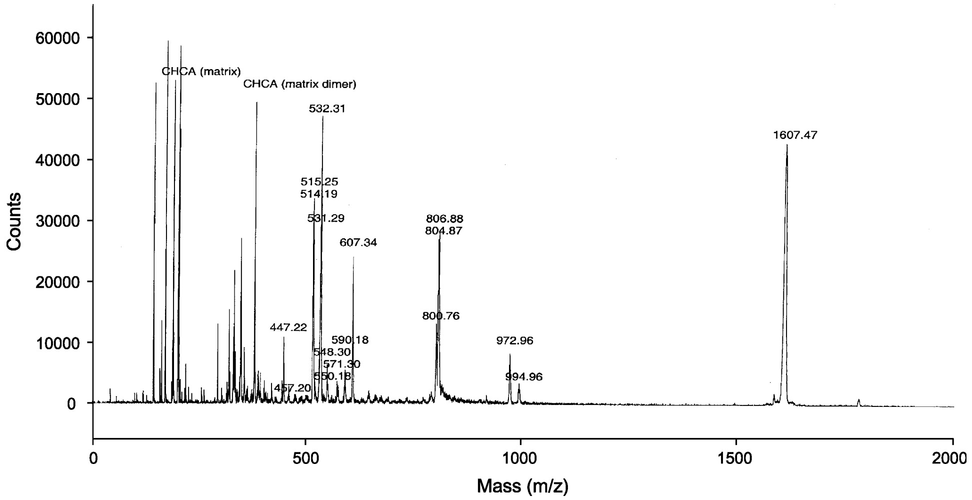
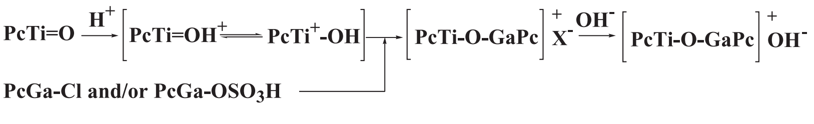


Fig. 2. TOF-MS spectrum of the product, carried out with equimolar Cl–GaPc(*t*-Bu)$_4$ and O=TiPc(*t*-Bu)$_4$ under the above mentioned conditions $[(t\text{-Bu})_4PcGa-O-TiPc(t\text{-Bu})_4]^+$ (entry 7 in Table 1).



Scheme 3. The proposal reaction mechanism to afford selective μ-oxo-bridged hetero-metal phthalocyanine dimmer.

Table 2
The TOF-MS results of various μ-oxo hetero-metal mixed dimer

Entry	X–MPc(Nc)	O=MPc(Nc)	Yield (%)	Calculated $[M-OH]^+/e$	Observed major peak
1	Cl–GaNc	O=TiPc	63.4	1358.87	1358.5
2	Cl–GaPc	O=TiNc	70.1	1358.87	1359.2
3	Cl–GaPc	O=VNc	82.1	1361.95	1362.9
4	Cl–AlPc	O=TiNc	76.1	1316.13	1315.7
5	Cl–GaPc(*t*-Bu)$_4$	O=TiNc	71.9	1583.30	1584.7
6	Cl–GaNc	O=TiNc	38.1	1559.11	1559.4

Pc: phthalocyanine, Nc: naphthalocyanine.

Goedken et al. [5] reported previously that μ-oxo-bridged titanium(IV) phthalocyanine dimer is stabilized by perchlorate anions and an asymmetrical stretching vibration of Ti–O–Ti in IR spectrum was at 820 cm^{-1}. These facts are considerably close to the data for (μ-oxo gallium phthalocyaninato) titanium phthalocyanine dimer, stabilized by hydroxyl ion.

Further characterization might be necessary for definitive structural information, like the previous work on μ-oxo aluminum phthalocyanine dimer, using X-ray diffraction analysis and AFM technology by Suga et al. [6].

2.2. OPC application

According to our initial motivation, we have studied the series of this derivative for the application as a photoreceptor and found that the product of entry 1, i.e. $[PcTi^+-O-GaPc]OH^-$, has high potentiality to be utilized as a CGM in OPC device. The electrostatic measurements were carried out with an electrostatic paper analyzer (model EPA-8200), manufactured by Kawaguchi Electric Works. The primary evaluation results are summarized in Table 3 and the spectral response of the photosensitivity is depicted in Fig. 4, in comparison with the authentic materials for a CGM, i.e. Y-form titany phthalocyanine [10] and μ-oxo gallium phthalocyanine dimer, reported in our previous work [1]. The product of the entry 1 in Table 1, i.e. $[PcTi^+-O-GaPc]OH^-$, has good characteristics to be utilized as a CGM with high to medium photosensitivity as shown in Table 3 and could be suitable for a laser–diode light source as well as the other phthalocyanine CGM as shown in Fig. 4. We also examined the durability of photosensitivity for 100 cycles of Carlson process and found much better than those of μ-oxo-bridged gallium phthalocyanine dimer, though inferior to Y-form titany phthalocyanine, as shown in Fig. 5.

3. Conclusion

In summary, it is strongly suggested that the reaction of the equimolar mixture of a halo-metal phthalocyanine derivative and an oxo-metal phthalocyanine derivative in concentrated sulfuric acid followed by treating in a basic solution gives selectively μ-oxo-bridged hetero-metal phthalocyanine dimer or the

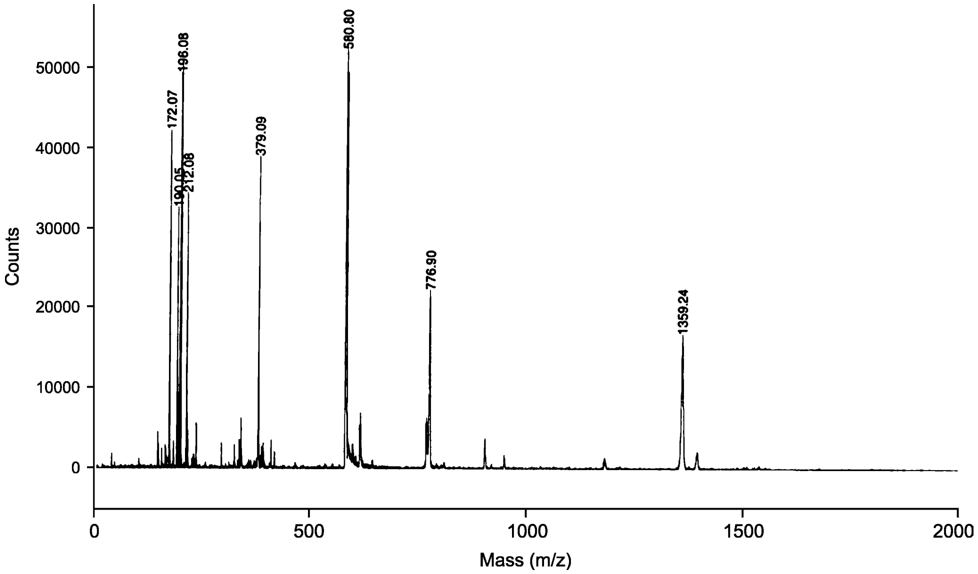
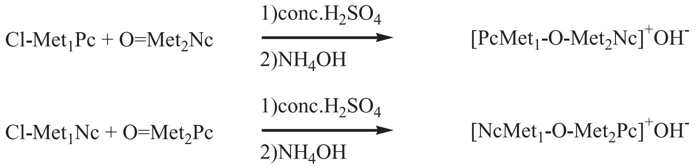


Fig. 3. TOF-MS spectrum of the product, carried out with equimolar Cl–GaPc and O=TiNc under the above mentioned conditions $[PcGa-O-TiNc]^+ = 1359.2$ (entry 2 in Table 2).



$$\text{Cl-Met}_1\text{Pc} + \text{O=Met}_2\text{Nc} \xrightarrow[\text{2)NH}_4\text{OH}]{\text{1)conc.H}_2\text{SO}_4} [\text{PcMet}_1\text{-O-Met}_2\text{Nc}]^+\text{OH}^-$$

$$\text{Cl-Met}_1\text{Nc} + \text{O=Met}_2\text{Pc} \xrightarrow[\text{2)NH}_4\text{OH}]{\text{1)conc.H}_2\text{SO}_4} [\text{NcMet}_1\text{-O-Met}_2\text{Pc}]^+\text{OH}^-$$

Scheme 4. Synthesis of μ-oxo hetero-metal Pc/Nc mixed dimmer.

Table 3
The primary photoconductive evaluation results

	Compound as CGM	Initial surface potential [V_{max}/V]	Dark decay ratio [DDR/%]	Photosensitivity potential [$E_{1/2}$/lx.s]	Residual [V_r/V]
1	[PcTi$^+$OGaPc]OH$^-$ [a]	−613.0	19.4	1.15	−17.0
2	μ−O−(GaPc)$_2$	−812.7	9.43	1.93	−22.0
3	Y−TiOPc [b]	−590.7	7.39	0.78	−7.0

Hydrazone compound was used for a CTM.
[a] The product is entry 1 in Table 1.
[b] This material was made followed by reference [10].

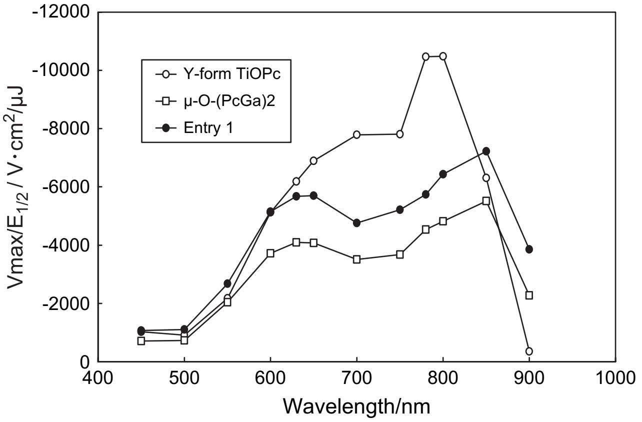


Fig. 4. Spectral response on the photosensitivity.

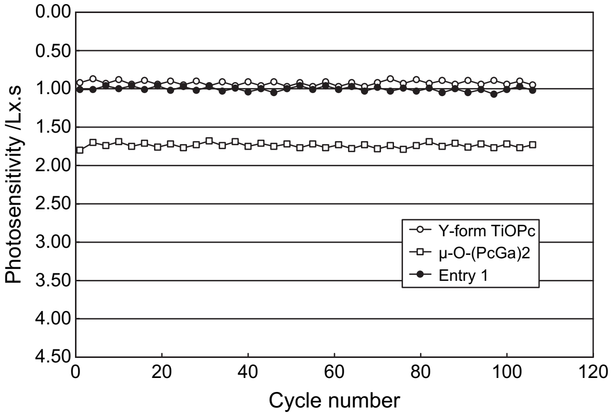


Fig. 5. Durability on the photosensitivity.

corresponding mixed dimer. And we have also showed that one of the products of this reaction has good characteristics for the photoreceptor. The synthetic method is accessible to be industrial and to afford enough purity to be utilized as a CGM in photoreceptor. The series of the products should possess high potentiality for high performance functional dyestuff, such as D−σ−A compound [7] for a non-linear optics [8], a sensitizer for solar cell, and so on. Further application will be described in elsewhere soon.

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