

Supporting Information of

**Macrocyclic Cu(II)-organophosphonate
building blocks**

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1. Synthesis

1.1 Materials and general procedures

2,7-dibromofluorene, triisopropylphosphite, tetrakis[triphenylphosphine]palladium(0), copper(II) sulfate pentahydrate, copper(II) chloride and 1,8-octanediphosphonic acid were purchased from Aldrich and 2,2'-bipyridine were purchased from Alfa-Aesar. They were used as received without any further purification. Hydrothermal reactions were carried out in a 23 ml polytetrafluoroethylene lined stainless steel containers under autogeneous pressure with distilled water.

1.2 Synthesis of (9H-fluorene-2,7-dyl)diphosphonic acid

The tetrakis[triphenylphosphine]palladium(0) catalyzed Michaelis-Arbuzov reaction was used to synthesize tetraisopropyl 9H-fluorene-2,7-dylbis(phosphonate). 2 g of 2,7-dibromofluorene (6.17 mmol) and 90 mg of Pd(PPh₃)₄ (0.078 mmol) were added to a 100 ml flask under argon atmosphere to prevent air and moisture from entering the reaction medium. 24 mL of triisopropylphosphite (97.34 mmol) was then added both as solvent and as reactive agent and the reaction temperature was gradually increased to 200 °C in 4 hours. While temperature was kept stable at 200 °C, 8 mL of triisopropylphosphite (32.45 mmol) and 90 mg of Pd(PPh₃)₄ (0.078 mmol) were added afterwards the temperature was gradually increased to 240 °C and reaction continued at this temperature for 96 hours. The reaction mixture was slowly cooled down to room temperature. The colourless solid product was crystallized. The colorless crystals

were filtered with a Gooch filter and washed with excess amount of n-hexane (yield; 2.47 g, 81 %). Spectral data: ^1H NMR (500 MHz, CDCl_3) δ 7.85 (m, 4H) , 7.54 (m, 2H), 4.02 (m, 4H), 3.96 (s, 1H), 1.28 (d, 8H).

The product of the Michaelis-Arbuzov reaction, tetraisopropyl 9H-fluorene-2,7-dylbis(phosphonate) (2.00 g, 4.04 mmol), was subjected to acidic hydrolysis with 37% HCl (35 mL). The reaction was carried out at 100° C. After 24 h, a white, intense mixture was obtained. In order to remove hydrochloric acid from the reaction mixture, 10 mL of methanol was added and then evaporated under vacuum. The final product was obtained as a white pure solid (Yield; 1.24 g, 94%). Spectral data: ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, 2H), 7.29 (s, 1H), 7.08 (d, 2H), 4.22 (s, 1H).

1.3 Synthesis of 1

A mixture of CuCl_2 (0.129 g, 0.96 mmol), 1,8-octanediphosphonic acid (0.120 g, 0.44 mmol), 2,2'-Bipyridine (0.080 g, 0.51 mmol) and water (10.084 g, 560 mmol) was stirred gently and heated to 200 °C for 24 h. After the reaction, the vessel was cooled to room temperature and precipitate part was filtered out by washing with acetone. Turquoise plates were obtained with another phase of long dark orange needles of $\text{Cu}(2,2'\text{-bpy})\text{Cl}$ 40 % yield based on 1,8-octanediphosphonic acid. Turquoise crystals of MOM1 were separated by hand picking for further experiments.

1.3 Synthesis of 2

A mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.120 g, 0.48 mmol), 2,2':6',2''terpyridine (0.072 g, 0.31 mmol), (9H-fluorene-2,7-dyl)diphosphonic acid (0.120 g, 0.37 mmol) and water (10.030 g, 557 mmol) was stirred gently and heated to 200 °C for 48 h. After the reaction, the vessel was cooled to room temperature and the precipitate was filtered out by washing with acetone. Green crystals were recovered with 82 % yield based on (9H-fluorene-2,7-dyl)diphosphonic acid.

2. Single crystal X-ray data collection and structure refinement

Unit cell measurements and intensity data collection was performed on an Bruker APEX II QUAZAR three-circle diffractometer using monochromatized Mo $\text{K}\alpha$ X-radiation ($\lambda = 0.71073$ Å). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS).¹ Space groups were determined using XPREP implemented in APEX2.² The structure was solved using the direct methods procedure in SHELXS-97³ and then refined by full-matrix least-squares refinements on F^2 using the SHELXL-97.³ All non-hydrogen atoms were refined anisotropically using all reflections with

$I > 2\sigma(I)$. Aromatic C-bound H atoms were positioned geometrically and refined using a riding mode. "Images generated using CrystalMaker[®]: a crystal and molecular structures program for Mac and Windows. CrystalMaker Software Ltd, Oxford, England (www.crystallmaker.com)"

Table S1. Crystal data and refinement parameters for **1** and **2**.

Structural formula or compound name	[{Cu(2,2'-bpy)} ₂ (HO ₃ P(CH ₂) ₈ PO ₃ H ₂) ₄] (1)	[{Cu(terpy)} ₂ (2,7-FDA-H ₂) ₂] · (2,7-FDA-H ₄)(2H ₂ O) (2)
Empirical formula	C ₅₂ H ₉₀ Cu ₂ N ₄ O ₂₄ P ₈	C ₆₉ H ₄₈ Cu ₂ N ₆ O ₂₃ P ₆
Formula weight	1530.11	1642.03
Temperature/K	299(2)	173. (2)
Crystal system	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	9.0492(5)	13.7108(12)
<i>b</i> /Å	9.6655(5)	14.8709(12)
<i>c</i> /Å	21.3503(11)	19.7110(18)
α /°	77.345(4)°	93.101(6)
β /°	78.084(4)°	104.443(5)
γ /°	69.959(4)°	102.318(5)
Volume/Å ³	1694.03(16)	3777.8(6)
<i>Z</i>	1	2
ρ_{calc} /g/cm ³	1.500	1.444
μ /mm ⁻¹	0.894	0.768
<i>F</i> (000)	800	1672
Crystal size/mm ³	0. × 0. × 0.0	0.20 × 0.12 × 0.11
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	2.95 to 25.25°	2.99 to 25.35
Reflections collected	15698	13788
Independent reflections	6272	8162
Data/restraints/parameters	6272 / 5 / 422	8162/0/962
Goodness-of-fit on <i>F</i> ²	1.099	0.965
Final <i>R</i> indexes [$I \geq 2\sigma(I)$]	<i>R</i> ₁ = 0.0446, <i>wR</i> ₂ = 0.1069	<i>R</i> ₁ = 0.0669, <i>wR</i> ₂ = 0.1641
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0497, <i>wR</i> ₂ = 0.1095	<i>R</i> ₁ = 0.1050, <i>wR</i> ₂ = 0.1774
Largest diff. peak/hole / e Å ⁻³	0.469 and -0.317 eÅ ⁻³	1.781/-0.681

3. Characterization

3.1 ICP-MS

In order to check the presence of any impurities in the crystal structure, we have run ICP-MS analysis. The results have shown that all of the transition elements except copper were not in the detectable range. ICP-MS was also run to see whether there is any palladium contamination in the structure originating from the palladium catalysts. It was also not detectable.

Table S2. ICP-MS Full quant table of 1.

Element	Mass	ISTD	Tune Mode	Conc	Units	RSD(%)	CPS	Ratio	Det	Time(sec)	Rep
Al	27	45	He	N.D	ppb	4.78	466.68	8.049E-03	Pulse	0.30	3
V	51	45	He	N.D	ppb	7.83	1,708.09	2.951E-02	Pulse	0.50	3
Cr	52	45	He	N.D	ppb	5.43	1,340.38	2.315E-02	Pulse	1.00	3
Mn	55	45	He	N.D	ppb	29.33	713.38	1.231E-02	Pulse	0.10	3
Fe	56	45	He	N.D	ppb	4.97	10,593.36	1.829E-01	Pulse	0.10	3
Co	59	45	He	N.D	ppb	14.44	1,113.42	1.917E-02	Pulse	0.10	3
Ni	60	45	He	N.D	ppb	2.15	27,715.15	4.785E-01	Pulse	1.00	3
Zn	66	72	He	N.D	ppb	11.24	5,000.85	1.088E-01	Pulse	0.10	3
As	75	72	He	N.D	ppb	12.83	83.67	1.814E-03	Pulse	1.00	3
Se	78	72	He	N.D	ppb	6.84	15.60	3.393E-04	Pulse	5.00	3
Ag	107	115	No Gas	N.D	ppb	5.16	2,046.86	7.634E-04	Pulse	0.10	3
Cd	111	115	No Gas	N.D	ppb	44.82	165.29	6.147E-05	Pulse	1.00	3
Cs	133	115	No Gas	N.D	ppb	2.33	2,316.92	8.637E-04	Pulse	0.10	3
Ba	137	115	No Gas	N.D	ppb	8.55	1,690.15	6.291E-04	Pulse	0.10	3
Pb	208	209	No Gas	N.D	ppb	1.82	59,203.02	1.550E-02	Pulse	0.10	3

Table S3. ICP-MS ISTD table of 1.

Tune Mode	Element	Mass	CPS	RSD(%)	ISTD Recovery%	Det	Time(sec)	Rep
He	Sc (istd)	45	57,945.52	2.40	95.0	Pulse	0.10	3
He	Ge (istd)	72	46,031.01	2.42	99.2	Pulse	0.10	3
No Gas	Rh (isdt)	103	2,503,124.03	0.22	101.2	Analog	0.10	3
He	Rh (isdt)	103	1,675,326.59	0.92	99.8	Analog	0.10	3
No Gas	In (istd)	115	2,683,366.91	2.25	100.0	Analog	0.10	3
No Gas	Lu (istd)	175	5,469,281.17	1.12	101.8	Analog	0.10	3
No Gas	Bi (istd)	209	3,819,877.44	0.64	102.2	Analog	0.10	3

3.2 TG Analysis

TGA experiment was carried out on a SII Nanotechnology-SII6000 Exstar TG/DTA 6300 model thermal analyzer instrument, with a heating rate of $^{\circ}\text{C min}^{-1}$ in an atmosphere of flowing N_2 from 25 to 900 $^{\circ}\text{C}$, Figure S1. The thermo gravimetric analysis (TGA) has shown that the molecule displays no weight loss up to ca. 210 $^{\circ}\text{C}$ indicating the absence of water molecules. **1** starts to decompose at ca. 210 $^{\circ}\text{C}$ and the decomposition continues until ca. 500 $^{\circ}\text{C}$.

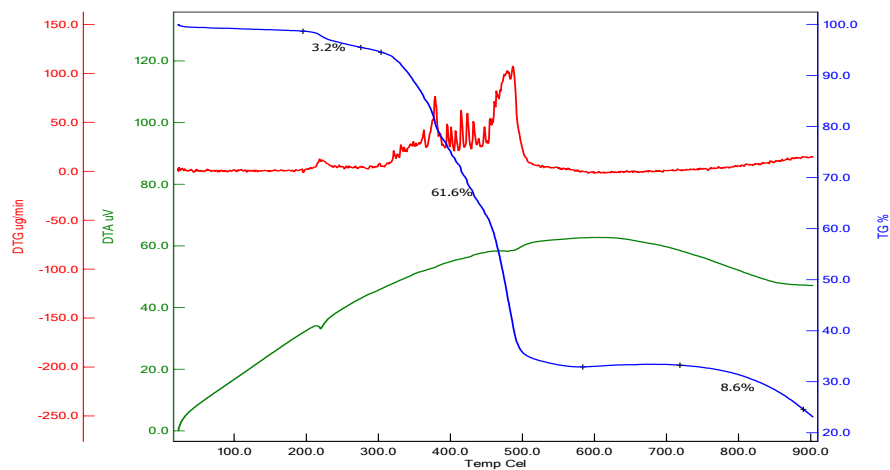


Figure S1. TG curve under N₂ atmosphere of compound **1**.

- [1] Bruker, SADABS, Bruker AXS Inc., Madison, Wisconsin, USA, **2005**.
[2] Bruker 2008, APEX2 (Version 2011.4-1), Bruker AXS Inc., Madison, Wisconsin, USA, **2008**.
[3] G. M. Sheldrick, Acta Crystallogr., Sect. A: Found. Crystallogr., **2008**, 64, 112–122.

