One-Dimensional Bis(dipyrrinato)zinc(II)-Linked Porphyrinatozinc(II) Polymer: Synthesis, Exfoliation Into Single Wires, and Photofunctionality

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Research Article

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One-dimensional Bis(dipyrrinato)zinc(II)-linked Porphyrinatozinc(II) Polymer: Synthesis, Exfoliation into Single Wires, and Photofunctionality

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Abstract

One-dimensional bis(dipyrrinato)zinc(II)-linked porphyrinatozinc(II) polymer, 2 were synthesized by facile metal complexation reaction between 5,15-bis(3,5-dioctyloxyphenyl)-10,20-bis(dipyrrinato)porphyrinatozinc(II), 1 and zinc(II) acetate. The bulky substituents on the porphyrin units allows 2 to be exfoliated into single molecular wires with a 2.8 nm height and 1.4 μm length. 2 exhibited promising photofunctionality derived from electronic interaction between bis(dipyrrinato)zinc and porphyrinatozinc(II) moieties, which can be engaged in energy transfer system such as photonic molecular wires.

Keywords: Coordination polymer, single molecular wire, porphyrin, dipyrrin complex, photo-electron conversion.

1 Introduction

Coordination polymers, whether one-dimension (1D), two-dimension (2D) or three-dimension (3D) based on their structures, can be synthesized basically in a very simple manner by a reaction of metal ions with bridging ligands in suitable solvents [1-2]. For years, 1D coordination polymers such as nanowires,[3-4] nanoribbons [5], nanofibers [6], nanorods [7] and so forth [8] play important roles in fabricating various nanoscale functional materials applicable to sensing [9], energy storage [10], and others [11-13]. In light harvesting application, porphyrin-based arrays are usually adopted due to their strong light absorption properties [14-15]. However, intense light absorption of porphyrins is generally limited only to the Soret band in the blue region. Subsequently, this became a limitation for porphyrins to be fully utilized in sun light harvesting. Therefore, hybridization between porphyrin and another pigment moiety is an efficient way to absorb the light over the whole visible region. Combination of porphyrin with dipyrrin has been studied [16-18]. Dipyrrin derivatives are bidentate ligands, easily coordinate with numerous divalent metal ions such as nickel(II), copper(II) and zinc(II) to afford bis(dipyrrinato)metal(II) which absorb and emit light intensely wherein highly useful in fabricating light-harvesting arrays as well as can act as emitting subunit in energy transfer system. Therefore, the integration of bis(dipyrrinato)zinc(II) with porphyrin building blocks are expected to display various photofunctions.
2 Experimental Details

2.1 Chemicals

All chemicals were purchased from Kanto Chemical Co., Tokyo Chemical Industry Co. Ltd or Wako Pure Chemical Industries Ltd, were used as received, unless otherwise stated. Pyrrol was purchased from Sigma-Aldrich and distilled under reduced pressure prior to use. Water was purified with a Milli-Q water system (Milipore Co.). 1 was synthesized according to previous literature studies with a few modifications.

2.2 Instrumentations

All $^1$H NMR data were recorded on a DRX500 (Bruker) using CDCl$_3$ as the solvent and tetramethylsilane ($\delta_{H} = 0.00$) as an internal standard. High-resolution fast atom bombardment mass spectrometry (HR-FAB-MS) was conducted using a JMS-700 MStation mass spectrometer (JEOL Ltd.). UV/vis spectra were obtained with a V-570 spectrometer (JASCO). Raman spectra were recorded using a NRS-5100 (JASCO). AFM measurements were carried out using an Agilent Technologies 5500 scanning probe microscope in the high-amplitude mode (tapping mode) with a silicon cantilever Nano World PPP-NCL probe. Photofunctionality of 2-modified SnO$_2$ was measured using a xenon lamp (MAX-302, Asahi Spectra Co., Ltd.) as photon flux source and a monochromator (CT-10, JASCO Corporation) to monochromate the photon flux. An electrochemical analyzer (ALS 750A, BAS Inc.) was used to control the electrode potential and photocurrent acquisition of the photoelectric conversion system. A photon counter (8230E and 82311B, ADC Corporation) was engaged in quantifying the photon flux of the incident light. All experiments were carried out under an ambient condition unless otherwise stated. The molecular size of 1 was estimated by DFT calculation. The DFT calculation was carried out using a Gaussian09 Revision D.01 program package. The geometry optimization was performed using B3LYP functional with the LANL2DZ basis set for Zn and 6-31g(d) basis set for the other atoms and the result was visualized using GaussView 5.0.8 software.

2.3 Synthesis of monomer, 1

A procedure for the synthesis of methyl 3,5-dioctylbenzoate$^1$ (L2)
The methyl ester L1 (6.92 g, 42 mmol) was dissolved in acetonitrile (300 mL). To this solution was added potassium carbonate (32.3 g, 233 mmol) and octylbromide (16 mL, 92 mmol). The mixture was heated under reflux for 48 hours. The precipitates in formal were filtered, and the filtrate was concentrated by a rotary evaporator. Unreacted octyl bromide was distilled off under reduced pressure. Yield: 12.7 g (32.4 mmol, 78 %)

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.18 (\text{d, } J = 2.4 \text{ Hz, 2H, Ar-2,6-H}), 6.65 (\text{t, } J = 2.4 \text{ Hz, 1H, Ar-4-H}), 3.99 (\text{t, } J = 6.6 \text{ Hz, 4H, octyloxy}), 3.89 (\text{s, } 3\text{H, Me}), 1.79 (\text{t-t, } J = 7.1 \text{ Hz, 4H, octyloxy}), 1.43 (\text{m, 4H, octyloxy}), 1.29 (\text{m, 16H, octyloxy}), 0.91 (\text{t, } J = 7.0 \text{ Hz, 6H, octyloxy}). \]

A procedure for the synthesis of 3,5-dioctyloxybenzyl alcohol (L3)

A solution of L2 (10 g, 26 mmol) in Et\(_2\)O (100 mL) was added to a suspension of LiAlH\(_4\) (1.16 g, 30.6 mmol) in Et\(_2\)O (100 mL) over 30 min. The reaction mixture was stirred overnight at RT. Hydrolysis by dropwise additions of H\(_2\)O (1.2 g) followed by 15% NaOH aq. solution (1.2 g) and more H\(_2\)O (3.6 g) gave a clear supernatant solution, which was separated from the salt. The organic layer was washed (2 × H\(_2\)O) and the combined aqueous layers extracted (2 × Et\(_2\)O). The combined organic layers were dried over MgSO\(_4\) and the solvent was evaporated to give a crude product containing L3 as a colorless oil (8.14 g, 22 mmol). Thereof was purified by flash column chromatography (eluent: CH\(_2\)Cl\(_2\)).

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 0.92 (\text{t, } J= 7.1, 6\text{H, } 2 \times \text{CH}_3), 1.21-1.49 (\text{m, } 20 \text{H, } 10 \times \text{CH}_2), 1.71-1.80 (\text{m, } 4\text{H, } 2 \times \text{CH}_2\text{CH}_2\text{O}), 1.65 (\text{t, } J= 6.1, 1\text{H, OH}), 3.97 (\text{t, } J= 6.6, 4\text{H, } 2 \text{CH}_2\text{O}), 4.64(d, J= 6.1, 2\text{H, CH}_2\text{OH}), 6.40 (\text{t, } J= 2.3, 1\text{H, 1H aromatic}), 6.52 (d, J= 2.3, 2\text{H, 2H aromatic}). \]
A procedure for the synthesis of 3,5-dioctyloxybenzaldehyde (L4)

[Chemical structure image]

Alcohol, L3 (8.14 g, 22 mmol) was dissolved in dry CH₂Cl₂ (60 mL). Sodium acetate (3.7 g, 44.6 mmol) was suspended in this solution, and the resultant suspension was cooled to 0 °C. Pyridinium chlorochromate (PCC) (10.6 g, 49 mmol) was carefully added to the suspension at 0 °C. After stirring for 2 hours, diethyl ether was added to the reaction mixture, and the liquid phase was separated by decantation. The residual gummy solid was washed with diethyl ether several times. The combined liquid phase was passed through a florisil short column. Diethyl ether was evaporated. The product was crystallized during evaporation. Colorless oil. Yield: 7.24 g (20 mmol, 90%)

¹H NMR (500 MHz, CDCl₃): δ 9.89 (s, 1H, CHO), 6.98 (d, J = 2.5 Hz, 2H, Ar-2,6-H), 6.70 (t, J = 4.5 Hz, 1H, Ar-4-H), 3.99 (t, J = 6.6 Hz, 4H, octyloxy), 1.80 (t-t, J = 7.1 Hz, 4H, octyloxy), 1.44 (m, 4H, octyloxy), 1.30 (m, 16H, octyloxy), and 0.89 (t, J = 7.0 Hz, 6H, octyloxy)

A procedure for the synthesis of 2-methylpyrrole

[Chemical structure image]

In a 100-mL round flask, KOH (8.9 g, 158 mmol) was dissolved in ethylene glycol. 2-formylpyrrol (3.0 g, 32 mmol) and hydrazine monohydrate (5 mL, 158 mmol) were added. The solution was stirred at 150 °C for 20 hours. After cooled to room temperature, the reaction mixture was diluted with 100 mL of water and then extracted with diethyl ether (10 mL × 6). The organic layer was washed with water (50 mL × 3) and dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The product was purified by distillation under reduced pressure (100 mmHg, 83 °C). Yield: 1.4 g (17.3 mmol, 53%).

¹H NMR (500 MHz, CDCl₃): δ 2.26 (s, 3H), 5.89 (s, br ,1H), 6.11 (dd, J = 3.0, 6.0 Hz ,1H), 6.62 (dd, J = 3.0, 4.5 Hz ,1H), 7.81 (s,1H)
A procedure for the synthesis of 2-(4′-Formylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane

Tetrahydrofuran (10 mL) and toluene (10 mL) were added to a mixture of a 4-formylphenyl boronic acid (0.89 g, 5.86 mmol) and pinacol (0.69 mg, 5.86 mmol). The mixture was concentrated to dryness under reduced pressure. The solvent addition and evaporation were repeated thrice, which afforded pure pinacolborane as white powder. Yield: 1.34 g (5.79 mmol, 99%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 10.06 (s, 1H), 7.97 (d, $J = 8.0$ Hz, 2H), 7.87 (d, $J = 8.5$ Hz, 2H), 1.37 (s, 12H)

A procedure for the synthesis of 4-methyl-2-[(2Z)-5-methyl-2H-pyrrol-2-ylidene](4-(tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)methyl)-1H-pyrrole, D1

A mixture of 2-methylpyrrole (3 mL, 35 mmol) and pinacolborane (3.7 mg, 16 mmol) was flushed with argon for 10 minutes and treated with trifluoroacetic acid (0.05 mL, 0.64 mmol). The mixture was stirred for 3 hours at room temperature and then p-chloranil (4.7 mg, 19 mmol) was added and the mixture was stirred for additional 5 minutes. Removal of solvent and excess pyrrole followed by chromatography (alumina, 100% CH$_2$Cl$_2$) afforded orange solid. Yield 3.62 g (15.6 mmol, 77%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 1.37 (s, 12 H), 2.44 (s, 6H), 6.17 (d, $J = 4.0$ Hz, 2H), 6.45 (d, $J = 4.0$ Hz, 2H), 7.49 (d, $J = 8.5$ Hz, 2H), 7.88 (d, $J = 8.0$ Hz, 2H)

HRMS (FAB$^+$); m/z calculated for C$_{23}$H$_{27}$BN$_2$O$_2$: 374.2166); found: 375.2227 [M+H]$^+$
A procedure for the synthesis of 5-(4-bromophenyl)dipyrromethane

Freshly distilled pyrrole (50 mL, 720 mmol) and 4-bromobenzaldehyde (5.33 g, 29 mmol) were added to a dry, round-bottomed flask and degassed with a stream of nitrogen for 5 minutes. Trifluoroacetic acid (0.22 mL, 2.8 mmol) was then added, and the solution was stirred under nitrogen at room temperature for 5 minutes before being quenched with 0.1 M NaOH. Ethyl acetate was then added. The organic phase was washed with water and dried over anhydrous Na$_2$SO$_4$, and the solvent was removed under vacuum to afford an orange-brown oil. The excess of pyrrole was recovered by vacuum distillation and the crude material was purified by flash column chromatography (eluent: SiO$_2$ hexane/ethyl acetate 90/10 $\rightarrow$ hexane/ethyl acetate 30/70) to afford yield: 3.9 g (13 mmol, 45%).

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 5.46 (s, 1H), 5.92 (s, 2H), 6.18–6.20 (m, 2H), 6.70–6.73 (m, 2H), 7.12 (d, 2H, J = 8.0 Hz), 7.47 (d, 2H, J= 8.5 Hz), 7.94 (br, s, 2H).

A procedure for the synthesis of 5,15-bis(3,5-dioctyloxyphenyl)-10,20-di(4-bromophenyl)porphyrinatozinc(II), P1

A solution of 3,5-dioctyloxybenzaldehyde (1.83 g, 5 mmol) and 5-(4-bromophenyl)dipyrromethane (1.5 g, 5 mmol) in dry CH$_2$Cl$_2$ (1.5 L) was stirred under Ar and the vessel was protected from light by aluminum foil. Trifluoroacetic acid (0.23 mL, 3.0 mmol) was added via syringe, and the resulting solution was stirred for 3 hours at room temperature. 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (1.70 g, 8 mmol) was added to the solution, and the resulting solution was stirred for an additional 2 hours. The reaction mixture was then neutralized by triethylamine and passed over an alumina column to remove polymeric materials. The solvent was removed by a rotary evaporator and a solution of Zn(OAc)$_2$ in methanol was added to a
solution of the free base porphyrin and the solution was stirred at room temperature during overnight. Yield: 13 mg (0.10 mmol, 2%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 0.89 (t, J=7.6 Hz, 12 H), 1.26-1.34 (m, 32H), 1.46 (m, 8H), 1.87 (t, J=7.1 Hz, 8 H), 4.13 (t, J=6.5 Hz, 8H), 6.90 (t, J=2.2 Hz, 2H), 7.39 (d, J=2.3 Hz, 4H), 7.92 (d, J=8.3 Hz, 4H), 8.10 (d, J=8.2 Hz, 4 H), 8.93 (d, J=4.6 Hz, 4H), 9.11 (d, J=4.6 Hz, 4H).

MALDI-TOF-MS m/z calculated for C$_{76}$H$_{90}$Br$_2$N$_4$O$_4$Zn: 1344.46; found: 1344.08

A procedure for the synthesis of 5,15-bis(3,5-dioctyloxyphenyl)-10,20-bis(dipyrrin)porphyrinatozinc(II), 1

Into a 20-mL glass vial with a stirbar were placed D1 (52.40 mg, 0.14 mmol), P1 (94.36 mg, 0.07 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (14.72 mg, 0.02 mmol), PPh$_3$ (79 mg, 0.30 mmol), K$_2$CO$_3$ (96.75 mg, 0.70 mmol) and dissolved in dimethylsulfoxide (15 mL) and H$_2$O (24 μL). The vessel was sealed by capping with an aluminium cap and the solution was degassed for 30 minutes before placed into the microwave cavity. Microwave irradiation of 300 W was used; the temperature being ramped from room temperature to 120 °C. Once the temperature reached the set point, the reaction mixture was held at this condition for 6 hours. After the mixture was allowed to cool at room temperature, the vessel was opened and the contents poured into a separating funnel. Water (100 mL × 5) was added and the organic layer was extracted by CH$_2$Cl$_2$ (3 × 50 mL) and drying over MgSO$_4$. The solution was concentrated under reduced pressure leaving the crude product. Yield: solid 13 mg (0.008 mmol,11%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 0.88 (t, J= 6.4 Hz, 12H), 1.26-1.49 (m, 40 H), 1.88 (m, 8H), 2.50 (s, 12H), 4.15 (t, J= 5.4 Hz, 8H), 6.26(d, J= 3.0 Hz, 4H), 6.67 (t, J= 3.8 Hz, 2H), 6.92 (t, J= 2.2 Hz, 4H), 7.73 (d, J= 8.1 Hz, 4H), 8.03 (d, J= 8.3Hz, 4H), 8.10 (d, J= 8.2Hz, 4H), 8.35 (d, J= 8.5 Hz, 4H), 9.10 (s, 4H). HRMS (ESI$^+$); m/z calculated for C$_{110}$H$_{120}$N$_8$O$_4$Zn: 1681.8802; found: 1681.8831 [M+H]$^+$

2.4 Preparation and Characterization of 1

In the present study, we fabricated new bis(dipyrrinato)zinc(II)-linked porphyrinic wires, 2 by simply mixing the 5,15-bis (3,5-dioctyloxyphenyl)-10,20-bis(dipyrrin) porphyrinatozinc(II), 1 in chloroform and zinc(II) acetate in methanol. The solution mixture was stirred at room
temperature for 30 hours and the resulting precipitate was filtered, washed with dichloromethane and methanol, then dried under reduced pressure to give bis(dipyrrinato)zinc(II) linked porphyrinatozinc(II) polymer wires, 2 as powdery solid. Upon ultrasonication 2 in toluene, the suspension exhibited Tyndall scattering once illuminated with green luminous flux, indicating the presence of nanoarchitecture in solution. The dispersibility of 2 was excellent in most organic solvents due to the presence of long alkoxy chain. Thus, the completion of metal complexation could be monitored by UV-vis spectroscopy. After ultrasonication, a solution of 2 in dichloromethane was dispersed on a highly ordered pyrolytic graphite (HOPG), and the atomic force microscopy (AFM) measurement was conducted. A topographic image in Fig. 1a displays several white lines with a length of 1.4 mm, of which height is 2.8 nm. This height is consistent with the optimized molecular structure of 1 calculated using density-functional theory (DFT) [21] shown in Fig. 1b.

![AFM topographic image](image1.png)

**Fig. 1** (a) AFM topographic image of HOPG modified with a dispersion of 2, (b) Size of 1 estimated by DFT calculation, (c,d) AFM cross-sectional profile along the blue lines.

Absorption bands for porphyrin; a strong Soret band at 428 nm and a Q band at 552 nm. In the spectrum of 2, one additional absorption peak appears at 493 nm, which is ascribed to the bis(dipyrrinato)zinc(II) moiety [19], confirming that the complexation between dipyrrin ligands and zinc(II) ions occurred successfully.
For bis(dipyrrinato)zinc(II)-linked porphyrinatozinc(II) wires, energy transfer from the bis(dipyrrinato)zinc moiety to the porphyrinatozinc(II) moiety is expected to occur when the bis(dipyrrinato)zinc moiety is excited at 493 nm because the Q band locates in the lower energy at 552 nm as shown in Fig. 2a. The exciton will transfer. This unique feature makes these wires as one of the possible candidates to be engaged in energy transfer system such as photonic molecular wires. Upon light irradiation, 1 exhibits fluorescence emission in the range of 500-700 nm as shown in Figure 2b. Two emission peaks appear at 601 nm and 648 nm owing to the porphyrin moiety. It should be noted that free dipyrrins generally emit very weak fluorescence [20]. The emission of 2 depends on the excitation wavelength. The excitation at 426 nm for the Soret band of the porphyrin moiety gives two emission peaks at 601 nm and 648 nm similar to 1. When irradiated at 493 nm for the excitation of the bis(dipyrrinato)zinc moiety, these two peaks appear, indicating the occurrence of energy transfer from the excited bis(dipyrrinato)zinc(II) moiety to the porphyrinatozinc(II) moiety. An additional peak is observed at 519 nm which is ascribed to the $\pi-\pi^*$ emission of the plain dipyrrinato ligands[18]. Photoluminescence quantum yields, $\Phi_{PL}$ of 1 and 2 when irradiated at 428 nm were 1.0% and 2.0%, respectively. Higher $\Phi_{PL}$ value of 2 than 1 would be the contribution of the luminescence from the porphyrinatozinc(II) moiety.
3 Results and Discussions

A photoelectron conversion system was fabricated using 2-modified SnO₂ as photoanode in an argon saturated 0.1 M Na₂SO₄ aq. containing 50 mM triethanolamine (TEAO) as an electron donating sacrificial reagent. The photoanode was prepared by casting the dispersion of 2 in dichloromethane on SnO₂. The photocurrent generation was observed when the bias potential more positive than 0.12 V vs. Ag/AgCl was applied to the working electrode. Figure 4 shows an action spectrum for the photocurrent at 0.12 V vs. Ag/AgCl, where the photo-response occurs over the whole range of 400-520 nm. This relatively wide range came from the hybridized structure of 2 composed of bis(dipyrrinato)zinc(II) and porphyrinatozinc(II). The quantum yield of photo-electron conversion was 0.19%, which is moderate but lower than the 2D polymer of bis(dipyrrinato)zinc(II) and porphyrinatozinc(II) hybrids [16] probably because of less efficient energy transfer pathways.

![Action spectrum for the photocurrent generation (blue dots) and the absorption spectrum of 2 on SnO₂ (orange solid line).](image)

The relationship between internal quantum efficiency (IQE) value and absorbance of 2 at 430 nm was studied by preparing several numbers of modified SnO₂ with 2. At lower absorbance value (0.05 and 0.06), IQE was recorded around 0.01% to 0.02%. Lower IQE values might cause by the smaller number of photons being absorbed by the sensitizer. As shown in Fig. 4, the quantum yield reached the maximal value with the absorbance at 0.098, at 430 nm. However, when the optical density reached beyond >0.1, the IQE decreased significantly. One possible reason is when the optical density of 2 is increased, the interaction with triethanolamine (TEOA) becomes more difficult and leads to restriction of electron donating from TEOA into the hole in the highest occupied molecular orbital of 2.
4. Conclusion

In conclusion, we successfully synthesized one-dimensional bis(dipyrrinato)zinc(II)-linked porphyrinatozinc(II) polymer wires by simple coordination reaction. The wires can be exfoliated into single molecular wires and exhibit photofunctionality based on the electronic interaction between the two complex units, which is utilizable for photoelectron conversion system.

Conflicts of interest

There are no conflicts to declare.

References

1. N.U. Parsekar, P.H. Bhargao, C. Näther, W. Bensch, B. R. Srivinasan, Synthesis and Structural Characterization of Three New Strontium(II) Coordination Polymers Based on 4-Nitrobenzoate. J Inorg Organomet Polym (2021). https://doi.org/10.1007/s10904-021-02097-9

2. M.S.Y. Parast, A. Morsali, Synthesis and Characterization of New Zinc(II) Coordination Polymer with a Flexible Hetro-coordination Ligand via In Situ Reaction as a New Precursor for Zinc(II) Oxide Nano-sphere Particles. J Inorg Organomet Polym 22, 998–1002 (2012). https://doi.org/10.1007/s10904-012-9691-y

3. P.-P. Sun, Y.-M. Li, , Y.-H. Zhang, H. Shi, F.-N. Shi, Application of a one dimensional Co-MOP wires o supercapacitors. Inorganica Chim. Acta. 521, 120337 (2021). https://doi.org/10.1016/j.ica.2021.120337

4. L. Xia, X. Xia, G. Zhang, J. Xu, R. Li, J. Dong, H. Wu, Two 1D Double-Chain Silver Coordination Polymer Constructed By Ag-Ag Bonds: Synthesis, Structure and Properties. J. Mol. Struct. 1236, 130286 (2021). https://doi.org/10.1016/j.molstruc.2021.130286

5. S. Maroufi, R. K.Nekouei, S. S.Mofarah, and V. Sahajwalla, Nanoscale Design of 1D Metal Oxides Derived From Mixed Ni-MH Battery/Transition Metal Dust. J. Hazard. Mater. 415, 125645 (2021). https://doi: 10.1016/j.jhazmat.2021.125645

6. S. Guo, Y. Li, C. Xue, Y. Sun, C. Wu, G. Shao, P. Zhang, Controllable Construction of Hierarchically CdIn2S4/CNFs/Co4S3 Nanofiber Networks Towards Photocatalytic
1. R. Takahata, T. Tsukuda, Ultrathin Gold Nanowires and Nanorods. Chem. Lett. 48, 906-915 (2019). https://doi.org/10.1246/cl.190313

2. H. Liu, DD Tang, XJ. Yan, Two Mixed-Ligand Co(II) Coordination Polymers: Treatment Activity on COPD via Reding the Activity of the AMPK Signaling Pathway. J Inorg Organomet Polym 31, 3793–3801 (2021). https://doi.org/10.1007/s10904-021-01996-1

3. N. R. Barveen, T.-J. Wang, Y.-H. Chang, Photochemical Synthesis of Ag/Au/AgCl Heterostructure From Ag Nanowires As A Reusable SERS Substrate For Ultrasensitive Detection of Analgesics and Antibiotics. Chem. Eng. J. 423, 130191 (2021). https://doi.org/10.1016/j.cej.2021.130191

4. F. Tao, Y. Liu, X. Ren, A. Jiang, H. Wei, X. Zhai, F. Wang, H-R. Stock, S. Wen, F. Ren, Carbon Nanotube-based Nanomaterials For High-Performance Sodium-ion Batteries: Recent Advances and Perspective. J. Alloys Compd. 873, 159742 (2021). https://doi.org/10.1016/j.jallcom.2021.159742

5. P. Zardari, A. Rostami, Construction of 1D Perovskite Nanowires by Urotropin Passivation Towards Efficient And Stable Perovskite Solar Cell. Sol. Energy Mater. Sol. Cells 227, 111119 (2021). https://doi.org/10.1016/j.solmat.2021.111119

6. L. Quan, X. Luo, L. Xue, J. Li, Y. Ouyang, Cu(II)-Coordination Polymer Nanostructures Induce Human Lung Cancer Cell Carcinoma Apoptotic Cell Death In Vitro and In Vivo. J Inorg Organomet Polym 30, 2744–2755 (2020). https://doi.org/10.1007/s10904-020-01483-z

7. A. Machín, K. Fontánez, J.C. Arango, D. Ortiz, J. De León, S. Pinilla, V. Nicolosi, F.I. Petrescu, C. Morant, F. Márquez, One-Dimensional (1D) Nanostructured Materials for Energy Applications. Materials 14, 2609 (2021). https://doi.org/10.3390/ma14102609

8. B. Du, D. Fortin, P.D. Harvey, A Conjugated Organometallic Polymer with Truxene Antennas as Side Arms, A Multiluminescent Material with Evidence for Intrachain MO Couplings. J Inorg Organomet Polym 23, 81–88 (2013). https://doi.org/10.1007/s10904-012-9718-4

9. S. Mustafar, K-H. Wu, R. Toyoda, K. Takada, H. Maeda, M. Miyachi, R. Sakamoto, H. Nishihara, Electrochemical Fabrication of One-dimensional Porphyric Wires on Electrodes. Inorg. Chem. Front. 3, 370-375 (2016). https://doi.org/10.1039/C5QI00239G

10. R. Sakamoto, T. Yagi, K. Hoshiko, S. Kusaka, R. Matsuoka, H. Maeda, Z. Liu, Q. Liu, W-Y. Wong, H. Nishihara, Photoactivity of Porphyrin-Hybridized Bis(dipyrrinato)zinc (II) Complex Micro- and Nanosheets. Angew. Chemie, 129, 3580 (2017). https://doi.org/10.1002/ange.201611785

11. T. Lazarides, G. Charalambidis, A. Vuillamy, M. Reglier, E. Klontzas, G. Froudakis, S. Kuhri, D. M. Guldi, A. G. Coutsolelos, Promising Fast Energy Transfer System Via An Easy Synthesis: Bodipy-Porphyrin Dyads Connected Via A Cyanuric Chloride Bridge, Their Synthesis, and Electrochemical and Photophysical Investigations. Inorg. Chem. 50, 8926-8936 (2011). https://doi.org/10.1021/ic201052k

12. A. N. Kursunlu, Porphyrin-Bodipy Combination: Synthesis, Characterization and Antenna Effect. RSC Adv 4, 47690-47696 (2014). https://doi.org/10.1039/C4RA09024A

13. S. Kusaka, R. Sakamoto, Y. Kitagawa, M. Okumura, H. Nishihara, An Extremely Bright Heteroleptic Bis(dipyrrinato)zinc (II) Complex. An Asian J. 7(5), 907-910 (2012). https://doi.org/10.1002/asia.201200131

14. Y. Ding, Y. Tang, W. Zhu, Y. Xie, Fluorescent and Colorimetric Ion Probes Based On
Conjugated Oligopyrroles. Chem. Soc. Rev. **44**, 1101 (2015).

21. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.