

Facile Preparation of Organometallic Nanorods from Various Ethynyl-Substituted Molecules

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A facile method to prepare one-dimensional (1D) organometallic nanomaterials from various ethynyl-substituted molecules is reported. The reactions of 3-chloro-1-ethynylbenzene, *p*-*t*Bu-phenylacetylene and 4-ethynylbiphenyl with Cu⁺ ions in acetonitrile yield nanorod-shaped copper acetylides (Cu–C≡C–R) crystals. In the case of linear alkynes, namely, propyne, 1-pentyne and 1-hexyne, it was found that using an

aqueous ammonia/ethanol mixed solvent instead of acetonitrile is a better approach to obtain 1D nanostructures. This procedure also enables us to prepare functional 1D nanomaterials. We demonstrate the preparation of a paramagnetic nanorod from the organic radical *p*-ethynylphenyl nitronyl nitroxide, and fluorescent nanorods from 9-ethynylphenanthrene and 2-ethynyl-9,9'-spirobifluorene.

1. Introduction

Anisotropic one dimensional (1D) and two dimensional (2D) nanomaterials, such as nanorods and nanosheets, have attracted significant attention in recent years due to their novel properties and various promising potential applications in the fields of energy storage,^[1] electronic and optoelectronic devices,^[2] photonic devices,^[3] antibacterial-materials,^[4] and chemical and biological sensors.^[5] To prepare anisotropic nanomaterials, various methods have been developed including chemical vapor deposition,^[6] thermal decomposition of precursors,^[7] template-assisted growth,^[8] swelling or exfoliation of layered materials^[9] and self-assembly of anisotropic materials.^[2a,c] Among these preparation methods, self-assembly is one of the most facile and amenable to mass-production for manufacturing anisotropic nanomaterials. On the other hand, the application of this method has been limited because the method needs high anisotropy such as anisotropic crystal structure,^[10] anisotropic templates^[11] or anisotropically adsorbed protective agent.^[12] Consequently, it is of great importance to develop a new self-assembly process to construct anisotropic nanostructures from various materials.

The purpose of the present work is to develop a new preparation method of 1D nanomaterials from various organic molecules. To achieve this goal, we focused on the anisotropic crystal structure of metal phenylacetylides (M–C≡C–Ph, M=Ag, Cu). The structure of M–C≡C–Ph is characterized by a polymeric ladder of M⁺ cations stabilized by anionic ethynyl groups (Figure 1),^[13] resulting in nanorod-shaped crystals.^[14] Another

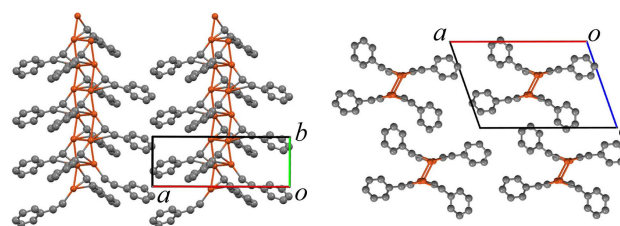


Figure 1. Crystal structure of Cu–C≡C–Ph viewed along the *c*- and *b*-axes.

important feature of M–C≡C–Ph is that the terminal phenyl group contributes little to the structural anisotropy. These structural features suggest that various organic molecules with ethynyl groups can naturally grow into 1D nanostructures when the molecules form metal acetylides, M–C≡C–R. This idea is supported by the fact that the reaction of 4-ethynyltoluene with Ag⁺ also gives 1D nanomaterials.^[15] In this paper, we report the preparation of copper acetylide nanorods from various ethynyl-substituted molecules (Figure 2).

2. Results and Discussion

The formation of copper acetylides was confirmed by elemental analyses and IR spectra. The stretching of ethynyl groups ($\nu_{C\equiv C}$) is shifted to lower frequencies by 130–200 cm⁻¹ when the molecules form copper acetylides.^[16] We used three methods to prepare 1D nanostructures. The first is the reaction of ethynyl-substituted organic molecules with Cu⁺ in acetonitrile. In the second method, an aqueous ammonia/ethanol mixed

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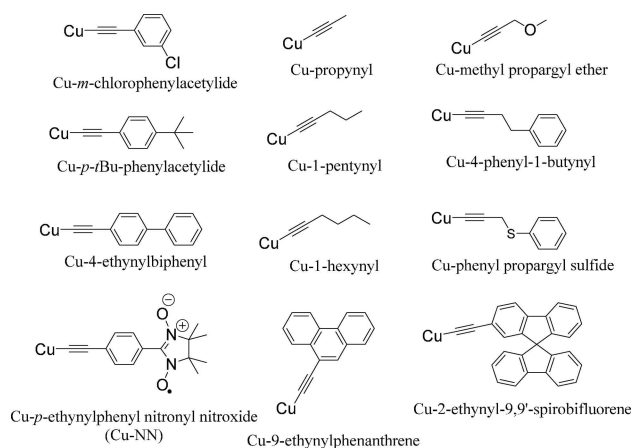


Figure 2. Molecular structures of Cu–C≡C–R.

solvent was used instead of acetonitrile. The method is suitable for highly soluble organic molecules such as 1-hexyne. The third is the recrystallization where slow crystal growth leads to longer 1D nanocrystals.

2.1. Ethynyl-Substituted Aromatic Molecules

Figure 3 shows the scanning electron microscopy (SEM) images of as-prepared Cu-*m*-chlorophenylacetylide, Cu-*p*-*t*Bu-phenylacetylide and Cu-4-ethynylbiphenyl. The nanorod-shaped acetylides were obtained by the reaction of Cu⁺ with ethynyl-

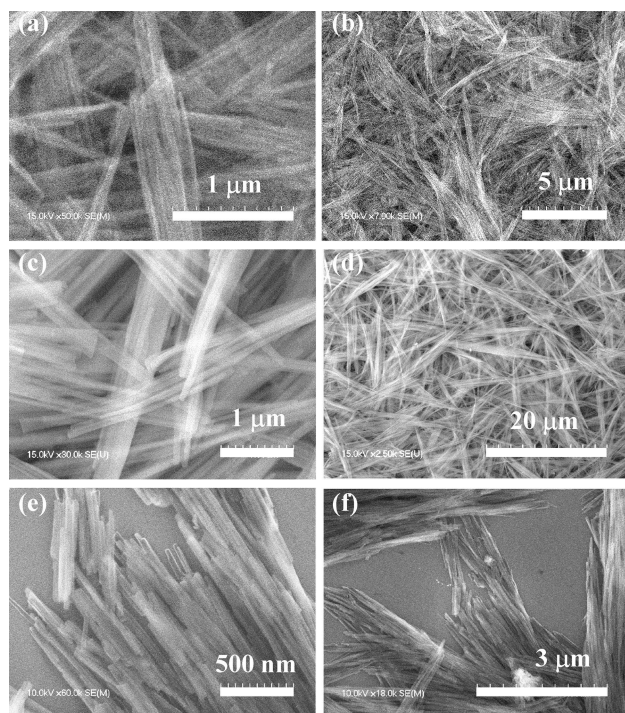


Figure 3. SEM images of Cu-*m*-chlorophenylacetylide (a, b), Cu-*p*-*t*Bu-phenylacetylide (c, d) and Cu-4-ethynylbiphenyl (e, f).

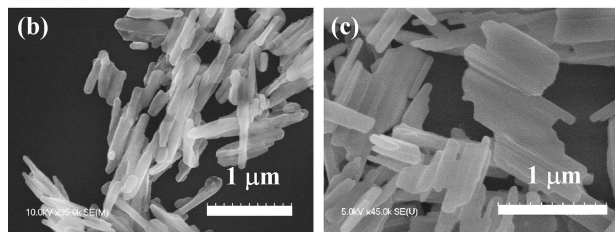
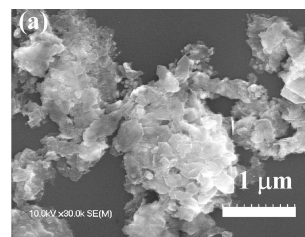


Figure 4. SEM images of Cu-propynyl (a), Cu-pentynyl (b) and Cu-hexynyl (c) prepared in acetonitrile.

substituted molecules. The observed diameters and lengths are 41 ± 8 nm and 4.8 ± 2.1 μ m for Cu-*m*-chlorophenylacetylide, 84 ± 18 nm and 12 ± 4.5 μ m for Cu-*p*-*t*Bu-phenylacetylide and 38 ± 10 nm and 1.7 ± 0.6 μ m for 4-ethynylbiphenyl.

2.2. Straight-Chain Alkynes

In contrast to the ethynyl-substituted aromatic compounds mentioned above, the reactions of propyne with Cu⁺ in acetonitrile yielded thin two-dimensional sheets as shown in Figure 4a. The sheet structure of Cu-propynyl is probably caused by the fusion of adjacent short nanorods, as observed in Cu-1-pentynyl and Cu-1-hexynyl (Figure 4b, c), which is a natural consequence of the higher solubilities of straight-chain alkynes in acetonitrile. In these cases, we found that using an aqueous ammonia/ethanol mixed solvent leads to better results, as shown in Figure 5. Cu-propynyl nanorods with a diameter of 48 ± 8 nm and a length of 2.4 ± 0.9 μ m were successively obtained from the mixed solvent. The mixed solvent also led to the formation of thinner and longer nanorods of Cu-1-pentynyl and Cu-1-hexynyl with diameters of 46 ± 9 and 60 ± 14 nm, and lengths of 2.6 ± 1.1 and 2.9 ± 1.0 μ m, respectively.

2.3. Recrystallization

In addition to using the mixed solvent, the recrystallization process is also useful for constructing 1D nanostructures, where the slow dissociation of PMe₃ from the soluble complex [Me₃P–Cu–C≡C–R] leads to slow crystal growth resulting in longer 1D nanocrystals of [Cu–C≡C–R].^[14a] We have successfully prepared nanorods of Cu-methyl propargyl ether, Cu-4-phenyl-1-butynyl and Cu-phenyl propargyl sulfide by recrystallization. Figure 6 shows the SEM images of the acetylides before and after recrystallization.

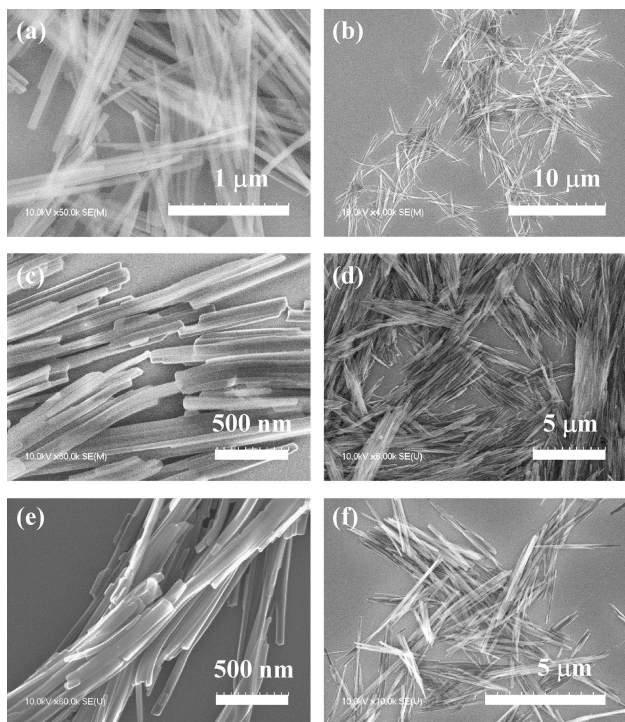


Figure 5. SEM images of Cu-propynyl (a, b), Cu-pentynyl (c, d) and Cu-hexynyl (e, f) prepared in the aqueous ammonia/ethanol mixed solvent.

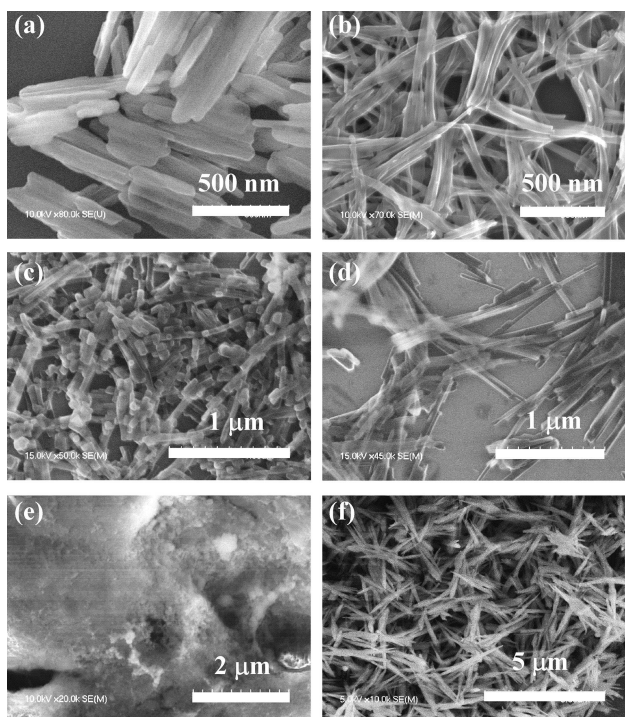


Figure 6. SEM images of Cu-methyl propargyl ether (a, b), Cu-4-phenyl-1-butynyl (c, d) and Cu-phenyl propargyl sulfide (e, f) before (a, c, e) and after (b, d, f) recrystallization.

The short and thick nanorods of Cu-methyl propargyl ether (Figure 6a) were converted by recrystallization into longer thin nanorods with diameters of 33 ± 6 nm and lengths of $690 \pm$

230 nm (Figure 6b). Recrystallized nanorods of Cu-4-phenyl-1-butynyl with a diameter of 56 ± 12 nm and a length of 900 ± 350 nm were also obtained from the as-prepared sample, which including a mixture of nanorods and nanoparticles as shown in Figure 6c and 6d. The most dramatic change was observed in the case of Cu-phenyl propargyl sulfide. Although the as-prepared material was a shapeless aggregate (Figure 6e), the recrystallization of Cu-phenyl propargyl sulfide led to 1D nanorods with a diameter of 89 ± 17 nm and a length of 1.5 ± 0.4 μm (Figure 6f).

2.4. Functional 1D Nanomaterials

In this section, we demonstrate the usefulness of our method for constructing functional 1D nanomaterials. We succeeded in constructing paramagnetic nanorods by using an ethynyl-substituted organic radical, *p*-ethynylphenyl nitronyl nitroxide (NN), as a ligand (Figure 7a). The diameter and length of the

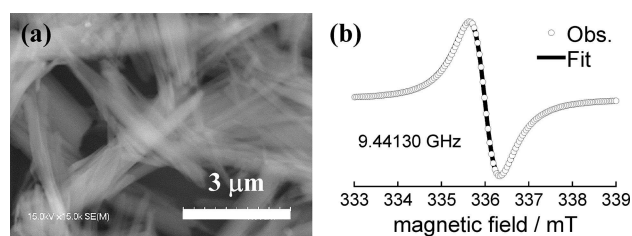


Figure 7. SEM image (a) and EPR spectrum (b) of Cu-NN. The solid line in (b) is the fit of the experimental data.

obtained nanorods are 115 ± 23 nm and 2.0 ± 0.8 μm , respectively. The powder electron paramagnetic resonance (EPR) spectrum of the nanorods exhibits a single-line signal as shown in Figure 7b. The spectrum is well fitted by a Lorentzian curve with a linewidth of $\Delta H_{pp} = 0.69$ mT and a *g*-value of 2.0077, which is consistent with the values of nitronyl nitroxide radicals.^[17] The magnetic susceptibility measurement also revealed the paramagnetic nature of the nanorods. The susceptibility obeys the Curie-Weiss law down to 1.8 K, with a Curie constant of 0.360 emu·K/mol and a Weiss temperature of -3 K. The observed Curie constant is in good agreement with the theoretical value of 0.375 emu·K/mol for $S = 1/2$, indicating that each *p*-ethynylphenyl nitronyl nitroxide molecule retains its radical character even in the nanorods.

Another example of functional 1D nanomaterials is fluorescent nanorods. Some cuprous clusters with acetylide ligands show photoluminescence,^[18] and we found that two kinds of copper acetylides, Cu-9-ethynylphenanthrene and Cu-2-ethynyl-9,9'-spirobifluorene, are fluorescent. Figure 8 shows SEM images of recrystallized Cu-9-ethynylphenanthrene and as-prepared Cu-2-ethynyl-9,9'-spirobifluorene nanorods with diameters of 68 ± 14 and 53 ± 13 nm and lengths of 1.2 ± 0.4 μm and 830 ± 340 nm, respectively. These nanorods emit orange light under UV irradiation as shown in Figure 9, where a broad emission

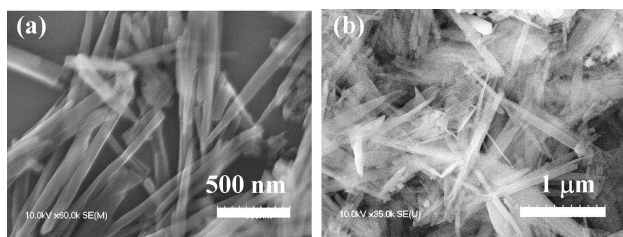


Figure 8. SEM images of recrystallized Cu-9-ethynylphenanthrene (a) and as-prepared Cu-2-ethynyl-9,9'-spirobifluorene (b).

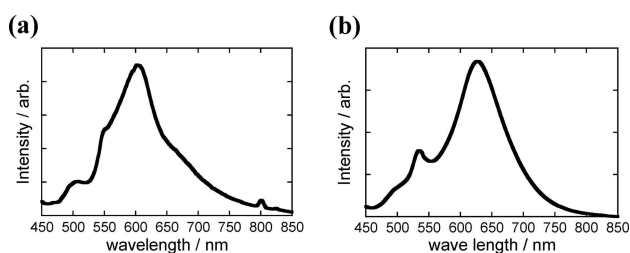


Figure 9. Fluorescence spectra of recrystallized Cu-9-ethynylphenanthrene (a) and as-prepared Cu-2-ethynyl-9,9'-spirobifluorene (b) (excitation: 400 nm)

was observed at around 605 nm for Cu-9-ethynylphenanthrene and 628 nm for Cu-2-ethynyl-9,9'-spirobifluorene.

2.5. Limitation of the Method and the Stability of Copper Acetylides

Although the preparation method of 1D copper acetylides is applicable for various organic molecules, we found that some amines are not suitable for this method. For example, Cu-*p*-ethynylaniline and Cu-*m*-ethynylaniline were obtained as 2D nanosheets and nanoparticles, respectively (Supporting Information Figure S8). Non-1D structures are probably caused by the strong interaction in a lateral direction mediated by amino groups, but the detail remains unclear.

The stability of the copper acetylides is also of importance. The obtained acetylides are air-stable over several months, and stable in water for at least a week. On the other hand, the acetylides gradually decompose into copper nanoparticles and polymerized ligands above ca. 50 °C. This instability originates from the strong reducing power of an ethynyl anion as observed in a silver acetylide.^[14a]

3. Conclusions

We have demonstrated the facile preparation of organometallic 1D nanomaterials. This method makes it possible to construct organometallic nanorods from various ethynyl-substituted organic molecules. The reaction of the ethynyl-substituted aromatic compounds *m*-chlorophenylacetylene, *p*-*t*Bu-phenylacetylene and 4-ethynylbiphenyl with Cu⁺ in acetonitrile yielded nanorods of copper acetylides, Cu–C≡C–R. Although

acetonitrile is not suitable for straight-chain alkynes due to their higher solubility, using an aqueous ammonia/ethanol mixed solvent leads to the nanorods of Cu-propynyl, Cu-1-pentynyl and Cu-1-hexynyl. In some cases, such as Cu-methyl propargyl ether, Cu-4-phenyl-1-butynyl and Cu-phenyl propargyl sulfide, recrystallization is the most appropriate method to obtain 1D nanostructures. This method also enables us to construct functional 1D nanomaterials such as paramagnetic nanorods of Cu-NN and fluorescent nanorods of Cu-9-ethynylphenanthrene and Cu-2-ethynyl-9,9'-spirobifluorene.

Experimental Section

Materials

m-Chlorophenylacetylene, *p*-*t*Bu-phenylacetylene, 4-ethynylbiphenyl, propyne, 1-pentyne, 1-hexyne, methyl propargyl ether, 4-phenyl-1-butyne, and phenyl propargyl sulfide are commercially available and were used without further purification. *p*-Ethynylphenyl nitronyl nitroxide,^[19] 9-ethynylphenanthrene^[20] and 2-bromo-9,9'-spirobifluorene^[21] were prepared according to the literature.

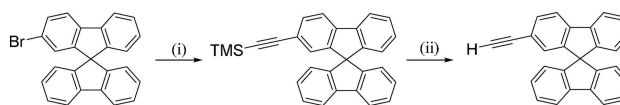
Synthesis of 2-Ethynyl-9,9'-Spirobifluorene

A solution of 2-bromo-9,9'-spirobifluorene (5.61 g, 14.2 mmol), CuI (0.24 g, 1.3 mmol) and Pd(PPh₃)₄ (0.84 g, 0.73 mmol) in a mixture of triethylamine (150 ml) and toluene (150 ml) was degassed by Ar bubbling for 30 min. Trimethylsilylacetylene (5.4 ml, 39 mmol) was added, and the mixture was stirred for 12 h at 70 °C under Ar atmosphere. The resulting solution was cooled and filtered. The residual was washed with hexane. The combined solution was evaporated and purified by flash chromatography (SiO₂, 2:1 hexane/dichloromethane). The obtained yellow powder (or oil) was dissolved in a mixture of MeOH (200 ml) and THF (200 ml). The solution was degassed, and KF (2.25 g, 38.7 mmol) was added. The reaction mixture was stirred for 24 h at r.t. The solvent was then evaporated and purified by chromatography (SiO₂, toluene, R_f = 0.84). The product was obtained as a white powder (4.02 g, 11.8 mmol, 83.1 %; see Scheme 1). Spectroscopic data were in accordance with those previously reported.^[22]

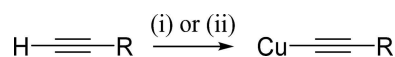
General Procedure for the Preparation of Copper Acetylide (Scheme 2)

Preparation in Acetonitrile

First, 0.55 g (2.9 mmol) of CuI was dissolved in 35 ml of acetonitrile. To the solution was added 3.0 mmol of ligand, followed by the slow addition of 0.63 ml (4.5 mmol) of triethylamine with vigorous stirring. After 1 h of stirring at room temperature, the solution was filtered and washed with acetonitrile followed by ethanol. The obtained powder was dried in vacuo.



Scheme 1. Synthesis of 2-ethynyl-9,9'-spirobifluorene. (i) CuI, Pd(PPh₃)₄, trimethylsilylacetylene, Et₃N + toluene. (ii) KF, MeOH + THF.



Scheme 2. Formation of copper acetylide. (i) CuI, Et₃N, acetonitrile. (ii) CuCl, NH₃aq + EtOH.

Cu-*m*-chlorophenylacetylide: Yellow powder (0.48 g, 83%). $\nu_{\text{C}\equiv\text{C}} = 1932 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -182 \text{ cm}^{-1}$). Anal. Calcd for C₈H₄Cl₁Cu₁: C 48.26, H 2.02%, Found: C 47.95, H 1.77%.

Cu-*p*-tBu-phenylacetylide: Yellow powder (0.46 g, 72%). $\nu_{\text{C}\equiv\text{C}} = 1909 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -197 \text{ cm}^{-1}$). Anal. Calcd for C₁₂H₁₃Cu₁: C 65.28, H 5.93%, Found: C 65.41, H 5.69%.

Cu-4-ethynylbiphenyl: Yellow powder (0.63 g, 90%). $\nu_{\text{C}\equiv\text{C}} = 1927 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -179 \text{ cm}^{-1}$). Anal. Calcd for C₁₄H₉Cu₁: C 69.84, H 3.77%, Found: C 69.76, H 4.05%.

Cu-propynyl: Yellow powder (0.23 g, 77%). $\nu_{\text{C}\equiv\text{C}} = 2034 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -126 \text{ cm}^{-1}$). Anal. Calcd for C₃H₃Cu₁: C 35.12, H 2.95%, Found: C 34.98, H 2.63%.

Cu-1-pentynyl: Yellow powder (0.28 g, 74%). $\nu_{\text{C}\equiv\text{C}} = 1939 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -181 \text{ cm}^{-1}$). Anal. Calcd for C₅H₇Cu₁: C 45.96, H 5.40%, Found: C 46.04, H 5.72%.

Cu-1-hexynyl: Yellow powder (0.36 g, 86%). $\nu_{\text{C}\equiv\text{C}} = 1926 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -200 \text{ cm}^{-1}$). Anal. Calcd for C₆H₉Cu₁: C 49.81, H 6.27%, Found: C 49.78, H 6.32%.

Cu-methyl propargyl ether: Yellow powder (0.31 g, 81%). $\nu_{\text{C}\equiv\text{C}} = 1924 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -200 \text{ cm}^{-1}$). Anal. Calcd for C₄H₅Cu₁O₁: C 36.22, H 3.80%, Found: C 36.47, H 4.03%.

Cu-4-phenyl-1-butynyl: Yellow powder (0.49 g, 88%). $\nu_{\text{C}\equiv\text{C}} = 1939 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -178 \text{ cm}^{-1}$). Anal. Calcd for C₁₀H₉Cu₁: C 62.32, H 4.71%, Found: C 61.99, H 4.55%.

Cu-phenyl propargyl sulfide: Yellow powder (0.55 g, 90%). $\nu_{\text{C}\equiv\text{C}} = 1944 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -176 \text{ cm}^{-1}$). Anal. Calcd for C₉H₇Cu₁S₁: C 51.29, H 3.35%, Found: C 50.98, H 3.46%.

Cu-NN: Green powder (0.62 g, 67%). $\nu_{\text{C}\equiv\text{C}} = 1971 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -127 \text{ cm}^{-1}$). Anal. Calcd for C₁₅H₁₆Cu₁N₂O₂: C 56.33, H 5.04, N 8.76%, Found: C 56.42, H 5.18, N 8.59%.

Cu-9-ethynylphenanthrene: Yellow powder (0.68 g, 89%). $\nu_{\text{C}\equiv\text{C}} = 1937 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -161 \text{ cm}^{-1}$). Anal. Calcd for C₁₆H₉Cu₁: C 72.58, H 3.43%, Found: C 72.21, H 3.60%.

Cu-2-ethynyl-9,9'-spirobifluorene: Yellow powder (0.76 g, 65%). $\nu_{\text{C}\equiv\text{C}} = 1942 \text{ cm}^{-1}$ ($\Delta\nu_{\text{C}\equiv\text{C}} = -162 \text{ cm}^{-1}$). Anal. Calcd for C₂₇H₁₅Cu₁: C 80.48, H 3.75%, Found: C 80.20, H 3.53%.

Preparation in an Aqueous Ammonia/Ethanol Mixed Solvent

Under an Ar atmosphere, 0.89 g (9.0 mmol) of CuCl was dissolved in a mixture of ethanol (50 ml), 28% NH₃aq (12.5 ml) and H₂O (45 ml). Then, 10 mmol of ligand dissolved in 5 ml of ethanol was added dropwise to the solution with vigorous stirring. After 1 h of stirring at room temperature, the solution was filtered and washed with 5% NH₃aq, H₂O, ethanol and diethyl ether. The obtained powder was dried in vacuo. The IR spectra of the obtained samples were identical to those of samples prepared in acetonitrile.

Cu-propynyl: Yellow powder (0.66 g, 71%). Anal. Calcd for C₃H₃Cu₁: C 35.12, H 2.95%, Found: C 34.81, H 2.60%.

Cu-1-pentynyl: Yellow powder (0.98 g, 83%). Anal. Calcd for C₅H₇Cu₁: C 45.96, H 5.40%, Found: C 45.62, H 5.15%.

Cu-1-hexynyl: Yellow powder (0.97 g, 74%). Anal. Calcd for C₆H₉Cu₁: C 49.81, H 6.27%, Found: C 49.59, H 6.06%.

General Procedure for the Recrystallization of Copper Acetylide

A 1 M solution of trimethylphosphine in THF (8.0 mmol, 8 ml) was added to a suspension of Cu-C≡C-R (6 mmol) in dichloromethane (50 ml). The solution was stirred for 1 h in the dark, and then the solution was filtered. The filtrate was evaporated without heating, and the precipitate was dissolved in a minimum amount of toluene. Then, the solution was diluted with 300 ml of appropriate solvent and incubated overnight. The precipitate of Cu-C≡C-R was filtered, washed with a small amount of ethanol and diethyl ether and dried in vacuo.

Cu-methyl propargyl ether: Diluted with acetonitrile, yellow powder (0.08 g, 10%). Anal. Calcd for C₄H₅Cu₁O₁: C 36.22, H 3.80%, Found: C 36.14, H 3.52%.

Cu-4-phenyl-1-butynyl: Diluted with acetone, yellow powder (0.15 g, 13%). Anal. Calcd for C₁₀H₉Cu₁: C 62.32, H 4.71%, Found: C 62.59, H 4.38%.

Cu-phenyl propargyl sulfide: Diluted with 1:1 toluene/chloroform, yellow powder (0.14 g, 11%). Anal. Calcd for C₉H₇Cu₁S₁: C 51.29, H 3.35%, Found: C 51.53, H 3.56%.

Cu-9-ethynylphenanthrene: Diluted with hexane, yellow powder (0.24 g, 15%). Anal. Calcd for C₁₆H₉Cu₁: C 72.58, H 3.43%, Found: C 72.77, H 3.69%.

Measurements

SEM images were acquired using a HITACHI FE-SEM S-4700 Type-II, where the sample was sonicated in ethanol and cast on a Si wafer. The EPR spectrum and magnetic susceptibility of Cu-NN were measured using a JEOL JES-TE200 X-band EPR spectrometer and a Quantum-Design MPMS-XL SQUID magnetometer, respectively. Fluorescence spectra of the powder samples of Cu-9-ethynylphenanthrene and Cu-2-ethynyl-9,9'-spirobifluorene were measured by a JASCO FP-8500 spectrometer with an integral sphere.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: alkyne ligands · copper · nanorods · organometallic nanomaterials · functional materials

- [1] a) B. Wang, Q. Ru, Q. Guo, X. Chen, Z. Wang, X. Hou, S. Hu, *Eur. J. Inorg. Chem.* **2017**, 2017, 3729–3735; b) Y. Wang, T. Wang, P. Da, M. Xu, G. Zheng, *Adv. Mater.* **2013**, *25*, 5177–5195; c) T. Ling, P. Da, X. Zheng, B. Ge, Z. Hu, M. Wu, X. Du, W. Hu, M. Jaroniec, S. Qiao, *Sci. Adv.* **2018**, *4*, eaau6261. d) S. M. Oh, S. B. Patil, X. Jin, S. Hwang, *Chem. Eur. J.*, **2017**, *24*, 4757–4773. e) J. Wang, J. Tang, B. Ding, V. Malgras, Z. Chang, X. Hao,

- Y. Wang, H. Dou, X. Zhang, Y. Yamauchi, *Nat. Commun.*, **2017**, *8*, 15717.
 f) B. P. Bastakoti, H. Huang, L. Chem, K. C. Wu, Y. Yamauchi, *Chem. Commun.*, **2012**, *48*, 9150–9152.
- [2] a) E. M. Garcia-Frutos, *J. Mater. Chem. C* **2013**, *1*, 3633–3645.; b) M. Sun, X. Zhang, Y. Zhong, C. Zhan, J. Yao, *Inorg. Chem.* **2016**, *55*, 13007–13013.; c) L. R. Fleet, J. Stott, B. Villis, S. Din, M. Serri, G. Aeppli, S. Heutz, A. Nathan, *ACS Appl. Mater. Interfaces* **2017**, *9*, 20686–20695. d) W. Feng, F. Qin, M. Yu, F. Gao, M. Dai, Y. Hu, L. Wang, J. Hou, B. Li, P. Hu, *ACS Appl. Mater. Interfaces*, **2019**, *11*, 18511–18516.
- [3] a) Y. Yan, C. Zhang, J. Yao, Y. S. Zhao, *Adv. Mater.* **2013**, *25*, 3627–3638.; b) Y. Ma, Q. Huang, T. Li, J. Villanueva, N. H. Nguyen, J. Fried, D. J. Sirbully, *ACS Photonics* **2016**, *3*, 1762–1767.
- [4] a) N. Dorosti, H. Mohammadpour, *Appl. Organomet. Chem.* **2018**, *32*, e4610. b) F. Perreault, A. F. Faria, S. Nejati, M. Elimelech, *ACS Nano*, **2015**, *9*, 7226–7236.
- [5] a) J. F. Fennel Jr., S. F. Liu, J. M. Azzarelli, J. G. Weis, S. Rochat, K. A. Mirica, J. B. Ravensbæk, T. M. Swager, *Angew. Chem. Int. Ed.* **2016**, *55*, 1266–1281; *Angew. Chem.* **2016**, *128*, 1286–1302.; b) X. Wang, K. Sun, S. Li, X. Song, L. Cheng, W. Ma, *ChemistrySelect* **2018**, *3*, 12871–12877. c) X. Yin, J. Cai, H. Feng, Z. Wu, J. Zou, Q. Cai, *New J. Chem.*, **2015**, *39*, 1892–1898.
- [6] Z. Zhan, L. Xu, J. An, H. Du, Z. Weng, W. Lu, *Adv. Eng. Mater.* **2017**, *19*, 1700101.
- [7] S. Heimann, W. Assenmacher, O. Prymak, S. Schulz, *Eur. J. Inorg. Chem.* **2015**, *2015*, 2407–2415.
- [8] M. Huang, Y. Zhang, F. Li, L. Zhang, R. S. Ruoff, Z. Wen, Q. Liu, *Sci. Rep.* **2014**, *4*, 3878.
- [9] a) F. Geng, R. Ma, Y. Ebina, Y. Yamauchi, N. Miyamoto, T. Sasaki, *J. Am. Chem. Soc.* **2014**, *136*, 5491–5500. b) F. Geng, R. Ma, A. Nakamura, K. Akatsuka, Y. Ebina, Y. Yamauchi, N. Miyamoto, Y. Takeyama, T. Sasaki, *Nat. Commun.* **2013**, *4*, 1632.
- [10] K. Judai, J. Nishijo, N. Nishi, *Adv. Mater.* **2006**, *18*, 2842–2846.
- [11] M. Müllner, T. Lunkenbein, M. Schieder, A. H. Gröschel, N. Miyajima, M. Förtsch, J. Breu, F. Caruso, A. H. E. Müller, *Macromolecules* **2012**, *45*, 6981–6988.
- [12] Y. Sun, B. Mayers, T. Herricks, Y. Xia, *Nano Lett.* **2003**, *3*, 955–960.
- [13] S. S. Y. Chui, M. F. Y. Ng, C. Che, *Chem. Eur. J.* **2005**, *11*, 1739–1749.
- [14] a) J. Nishijo, O. Oishi, K. Judai, N. Nishi, *Chem. Mater.* **2007**, *19*, 4627–4629.; b) H. Jiang, P. Zhou, Y. Wang, R. Duan, C. Chen, W. Song, J. Zhao, *Adv. Mater.* **2016**, *28*, 9776–9781.
- [15] K. Judai, Y. Hatakeyama, J. Nishijo, *J. Nanosci.* **2013**, *2013*, 545430.
- [16] a) Y. L. Chow, G. E. Buono-Core, *Can. J. Chem.* **1983**, *61*, 795–800.; b) Y. Okamoto, S. K. Kundu, *J. Phys. Chem.* **1973**, *77*, 2677–2680.
- [17] a) L. Li, S. Liu, Y. Zhang, W. Shi, P. Cheng, *Dalton Trans.* **2015**, *44*, 6118–6125.; b) M. Nishizawa, D. Shiomi, K. Sato, T. Takui, K. Itoh, H. Sawa, R. Kato, H. Sakurai, A. Izuoka, T. Sugawara, *J. Phys. Chem. B* **2000**, *104*, 503–509.
- [18] P. C. Ford, E. Carianti, J. Bourassa, *Chem. Rev.* **1999**, *99*, 3625–3647.
- [19] C. Rajadurai, V. Enkelmann, G. Zoppellaro, M. Baumgarten, *J. Phys. Chem. B* **2007**, *111*, 4327–4334.
- [20] S. Grunder, D. M. Torres, C. Marquardt, A. Błaszczuk, R. Krupke, M. Mayor, *Eur. J. Org. Chem.* **2011**, *2011*, 478–496.
- [21] S. O. Jeon, K. S. Yook, C. W. Joo, H. S. Son, J. Y. Lee, *Thin Solid Films* **2010**, *518*, 3716–3720.
- [22] T. Takata, F. Ishiwari, T. Sato, R. Seto, Y. Koyama, *Polymer J.* **2008**, *40*, 846–853.

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