Synthesis of Click-Chelator via Cu(I)-Catalyzed Alkyne-Azide Cycloaddition

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The click-ligands based on 1,2,3-triazole and pyridine unit has been synthesized via Cu(I)-catalyzed alkyne-azide cycloaddition from corresponding organic azides and terminal alkynes. The ligand structure was characterized by NMR, IR and elemental analysis as well as single crystal diffractions. The single crystal structure of the complexes from two different ligands coordinating to Cu(II) and Co(II) ions indicated that the N(2) atom in 1,2,3-triazole unit can act as an efficient donor to metals through the rational molecular design.

Keywords Click Chemistry, ligand design, N ligands, synthesis

Introduction

Since the birth of coordination chemistry in 1896, searching for new kind of ligands has drawn a continuous attention. Especially, the multi-dentate chelating ligand as the building block plays a crucial role in constructing different types of supramolecular structure and can also be used to prepare variety kinds of functional materials.[1] However, design of new ligand is still sometimes a challenge to the chemist due to the multi-step synthesis and rigorous synthetic conditions. Recently, the "Click Reaction" firstly introduced by Sharpless and co-workers affords a good way to achieve this target.[2] Among them, the Cu(I)-catalyzed alkyne-azide [3+2] cycloaddition (CuAAC reaction) is a typical one to synthesize the 1,4-disubsituted-1,2,3-triazoles. Due to its much mild reaction conditions, well-easily experimental manipulation, high efficiency and excellent regio-selectivity,[3] it has been widely used in many areas such as molecular biology, supramolecular assembly, new medicine design, nano-optoelectronics and materials science.[4] In these applications 1,2,3-triazole only acts as a simple linkage. As a stable aromatic heterocycle, the 1,2,3-triazole also contains two nitrogen atoms [N(2) and N(3)] with one pair of non-covalent electrons, indicating both of them can act as donors to coordinate with different metals.[3] Recent research revealed that N(3) atom of 1,2,3-triazole unit did take part in the coordination with metal,[4,5] which was confirmed by single crystal analysis. So 1,2,3-triazole-based ligands from CuAAC reaction have been applied in catalyst, radio-active labeling medicines, organometallics,[5-12] *etc*.

In addition, the theoretical calculation revealed that N(2) atom in 1,2,3-triazole has much lower electron density than N(3), indicating that N(2) atom is not a good coordinating site compared to N(3), which was also supported by some experimental results.[10-13] Since N(2) atom has an electron pair as well, it can also coordinate to metal via rational molecular design. Thus, synthesis of new 1,2,3-triazole-based ligands and study on the coordinate ability of N(2) atom in 1,2,3-triazole deserve to be further attempted, which will expand the coordination chemistry or supramolecular chemistry of 1,2,3-triazole-based ligands. So we synthesized a series of click-ligands based on 1,2,3-triazole and pyridine group via CuAAC reaction and also obtained several Cu(II) or Co(II) metal complexes from two simple ligands, 2-[(4-phenyl-*1H*-1,2,3-triazol-1-yl)methyl] pyridine (**3a**) and 4-[(4-phenyl-*1H*-1,2,3-triazol-1-yl)-methyl] pyridine (**3c**). The crystal data indicated that the N(2) atom of 1,2,3-triazole can efficiently participate in the coordination to metals through the molecular design of "chelate effect".[1]

Results and discussion

Synthesis

The synthetic routes for the click-ligands are shown in Schemes 1—3. All the azides used in CuAAC reaction were synthesized via the classical S_N2 reaction from 2, 3, or 4-(chloromethyl)pyridine with sodium azide in acetonitrile.[14] The alkynes were prepared through Pd(0)-catalyzed Sonogashira coupling from the corresponding bromo- or iodine-aromatic compounds and ethynyl-

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trimethylsilane.[15] The CuAAC reaction was carried out in a typical procedure described in reference,[3] in which *in-situ* generated Cu(I) cation had been employed as catalyst and excess azides was applied to ensure the full conversion of alkyne component. In each reaction, 2% molar ratio of the catalyst and 10% molar ratio of the reducing reagent in aqueous solution (fresh-generated sodium ascorbate) had been added. The excess ascorbate can prevent the oxidation of Cu(I) to Cu(II) ion.[3] The starting materials including mono-, bis- or tri-alkynes was employed to prepare different multi-dentate chelate ligands. It was found that compounds **4a**—**4c** can precipitate from the reaction system during the reaction due to their low solubility in common solvents. Thus, considering solubility of the different products as well as starting compounds, THF was utilized instead of *t*-BuOH in the synthesis of compounds **5a**—**8**.

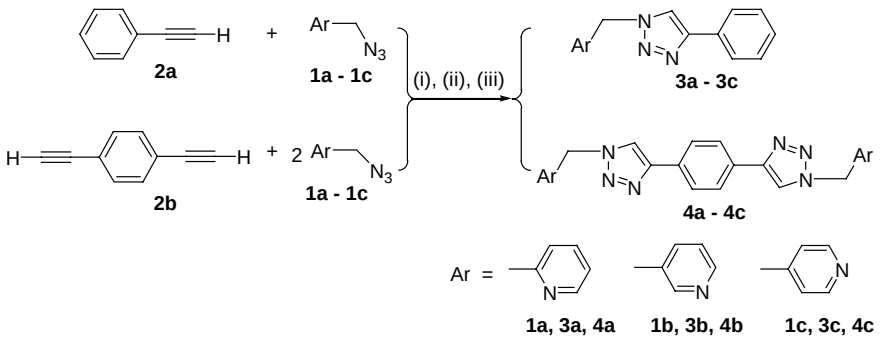
Generally, the reaction mixture had been kept stirring smoothly under 50 ℃ for 12 h to make sure that all alkynes were converted to products. They were purified by chromatography with different eluent and obtained in high yields (except for compounds **4a**—**4c**, the relatively low yields are due to poor solubility in common organic solvents). So the long-chain alkyl group was introduced into the click-chelators to improve the solubility, which can possibly affect the final assembly results with metals.

Crystal sructures[16]

The substituted group at N(1) atom of 1,2,3-triazole in **3a** is 2-methylpyridine, which can co-coordinate to metal with nitrogen atom of pyridine (N_{py}) to form a six-membered chelate ring. However, in **3b** and **3c** the substituted group is 3-methylpyridine and 4-methylpyridine respectively, so both of them can hardly form stable chelating ring with metal. In order to investigate the coordinating ability of N(2) atom in different kinds of liagnds, we selected **3a**—**3c** to react with $CuCl_2$ at same reaction condition. Two complexes, Cu(II)-**3a**[17] and Cu(II)-**3c**, had been obtained and their crystal structures were determined as in Figures 1 and 2, respectively. The corresponding complex of **3b** was not obtained, although it had been tried for several times with different synthetic routes.

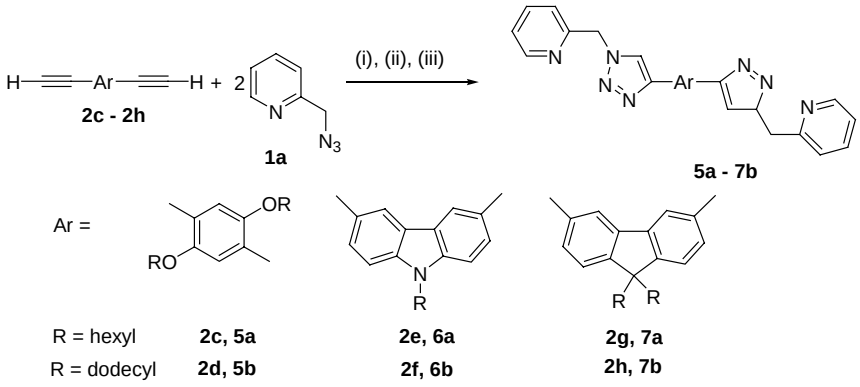
As expected, the N(2) atom did co-coordinate to the metals with N_{py} atom to form the stable six-membered chelate ring in Cu(II)-**3a**. While in Cu(II)-**3c** only N_{py} atom coordinated to Cu(II) ion, in which N(2) and N(3) of 1,2,3-triazole unit did not participate the coordination. In Cu(II)-**3a**, Cu(II) is in a distorted octahedral geometry, in which the bond distance between Cu(II) and N_{py} is 2.040 Å and the bond distance of N(2) and Cu(II) is

Scheme 1 Synthetic routes for **3a**—**3c** and **4a**—**4c**



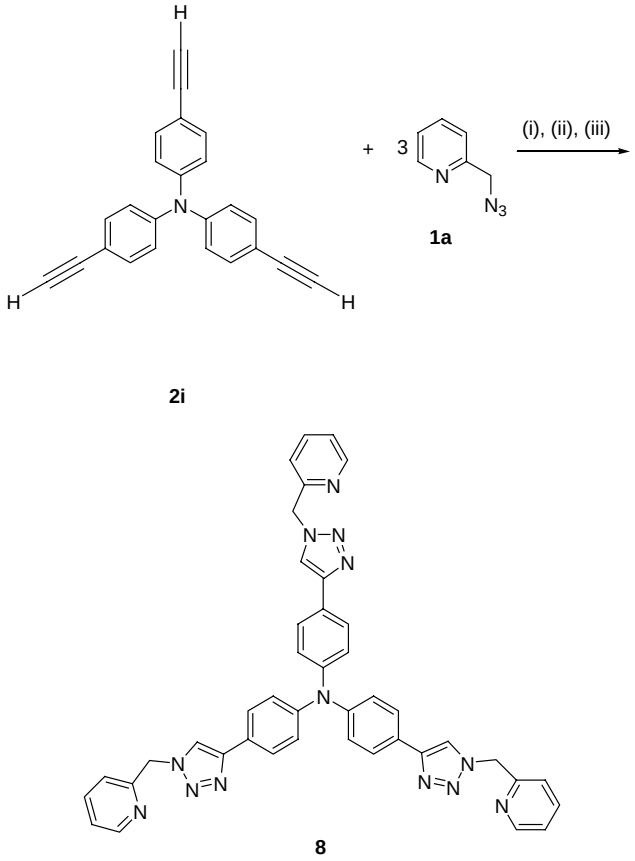
(i) 2 mol% $CuSO_4$•$5H_2O$, 10 mol% $NaHCO_3$,10 mol% ascorbic acid; (ii) *t*-BuOH/H_2O (*V*/*V*＝1/1); (iii) 50 ℃, 12 h.

Scheme 2 Synthetic route for **5a**—**7b**



(i) 2 mol% $CuSO_4$•$5H_2O$, 10 mol% $NaHCO_3$,10 mol% ascorbic acid; (ii) THF/H_2O (*V*/*V*＝2/1); (iii) 50 ℃, 12 h.

Scheme 3 Synthetic route for **8**



(i) 2 mol% $CuSO_4$•$5H_2O$, 10 mol% $NaHCO_3$,10 mol% ascorbic acid;; (ii) THF/H_2O (*V*/*V*=2/1); (iii) 50 ℃, 12 h.

2.715 Å. The difference of 0.675 Å between two Cu(II)—N bonds indicates that the coordinating ability of N(2) atom is much weaker than that of N_{py} in Cu(II)-**3a**.

Table 1 Reactants and separation condition for the click-ligands

No.	Azide	Alkyne	Eluent	Yield%
3a	**1a**	**2a**	Ethyl acetate/Petroleum (*V*/*V*=2/1)	80
3b	**1b**	**2a**	Ethyl acetate	85
3c	**1c**	**2a**	Ethyl acetate	88
4a	**1a**	**2b**	DCM/Methanol (*V*/*V*=18/1)	51[a]
4b	**1b**	**2b**	DCM/Methanol (*V*/*V*=18/1)	49[a]
4c	**1c**	**2b**	DCM/Methanol (*V*/*V*=10/1)	50[a]
5a	**1a**	**2c**	DCM/Methanol (*V*/*V*=18/1)	70
5b	**1a**	**2d**	DCM/Methanol (*V*/*V*=18/1)	94
6a	**1a**	**2e**	DCM/Methanol (*V*/*V*=18/1)	81
6b	**1a**	**2f**	DCM/Methanol (*V*/*V*=18/1)	93
7a	**1a**	**2g**	DCM/Methanol (*V*/*V*=18/1)	94
7b	**1a**	**2h**	DCM/Methanol (*V*/*V*=18/1)	92
8	**1a**	**2i**	DCM/Methanol (*V*/*V*=18/1)	90

[a] The low yields of **4a**—**4c** were due to their poor solubility in the solvent used as eluent.

In order to further study the coordinating ability of N(2) atom with different metals, another complex of Co(II)-**3a** was obtained and its crystal structure is shown in Figure 3. It showed similar coordination geometry to Cu(II)-**3a**. The bond distance between Co(II) ion and N(2) is 2.196 Å and the bond distance between Co(II) and N_{py} is 2.185 Å. The difference between two Co—N bonds is only 0.011 Å, indicating that N(2) atom exhibits comparable coordinating ability with N_{py}. From above results of Cu(II)-**3a** and Co(II)-**3a**, it can be seen that the coordinating ability of N(2) atom in 1,2,3-triazole is different when it coordinates to different metals. Therefore, it can be concluded that the coordi-

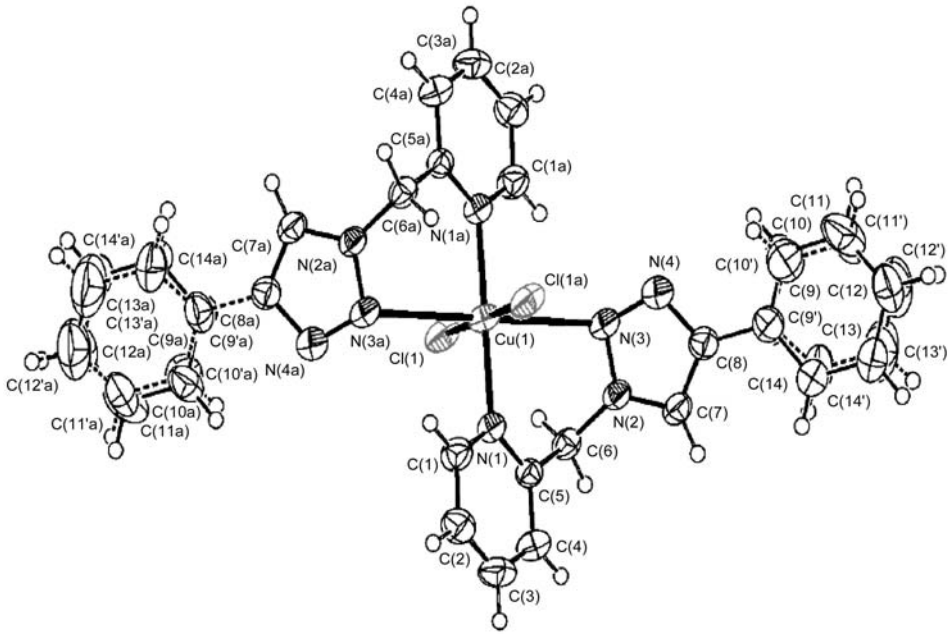


Figure 1 Crystal structure of Cu(II)-**3a**.

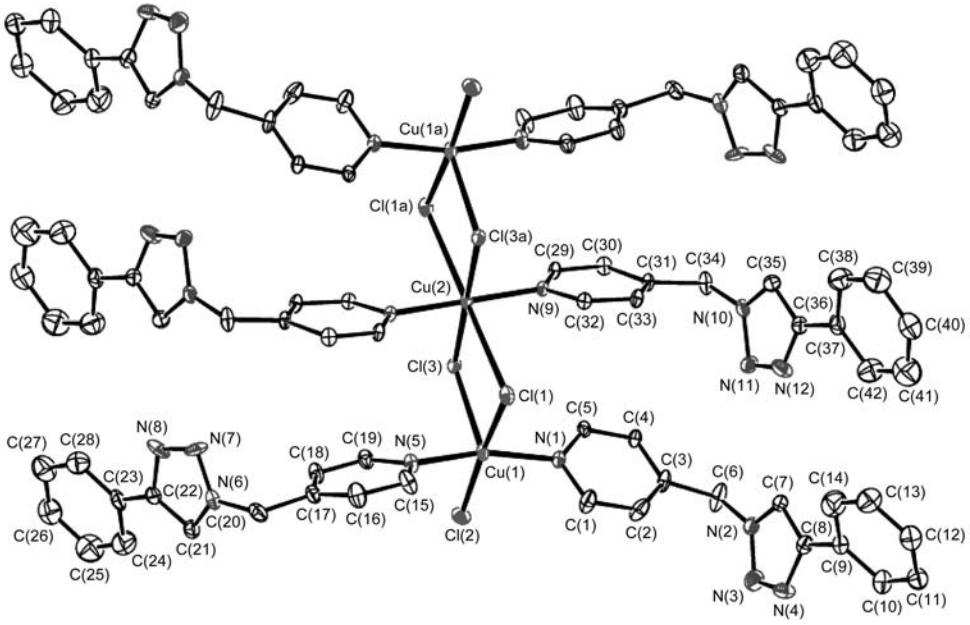


Figure 2 Crystal structure of Cu(II)-**3c** (the water has been omitted for clarity).

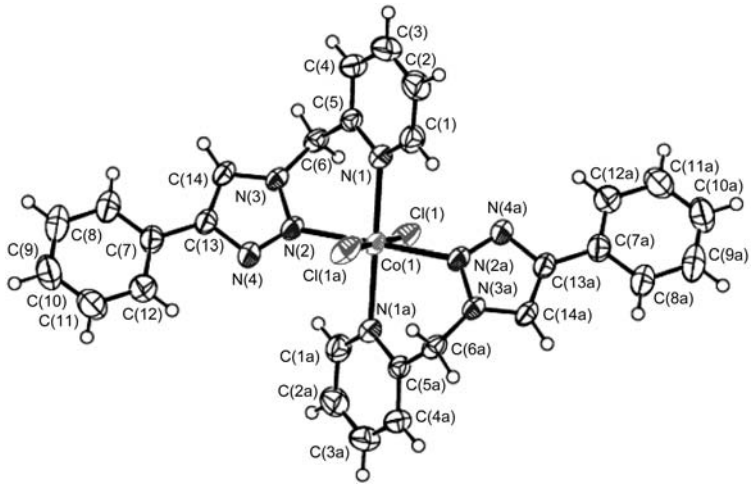


Figure 3 Crystal structure of Co(II)-**3a**.

nating ability of N(2) atom of 1,2,3-triazole in different type of ligands such as **3a**—**3c** is much different, and its coordinating ability is also different when it coordinates to different metals. And the N(2) atom can act as an effective donor to metal via the rational molecular design such as "chelate effect".

At same time, single crystal of **5a** was obtained by slow diffusion of methanol to its dichloromethane solution and its crystal structure was determined with X-ray diffraction method as shown in Figure 4. It can be seen that the N(2) atom of 1,2,3-triazole and N_{py} atom in 2-pyridine adopt a "U" shape conformation that will form a stable six-membered chelate ring when they coordinate with the metal ions. This supports the above research results.

Obviously, the position of N_{py} atom in pyridine unit greatly affects the coordinating ability of N(2) atom in this kind of click-ligands. Thus, a series of new multi-chelating click-ligands such as **5a**, **5b**, **6a**, **6b**, **7a**, **7b** and **8** based on the structure of **3a** are designed and synthesized. Their coordination with different metals is in progress.

Conclusion

Via Cu(I)-catalyzed click reaction a series of ligands based on 1,2,3-triazole unit have been designed and synthesized. All these ligands can be easily prepared in high yields and their structures have been characterized by NMR, IR, MS and elemental analysis. Three complexes from ligands **3a** and **3c** have been obtained and the crystal structure was determined, which confirmed that the N(2) atom in 1,2,3-triazole unit can act as an effective donor to coordinate with metals via the rational molecular design. The coordination behaviors of these ligands are now under further investigation, which may be applied in organic-inorganic hybrid opto-electronic materials in the future.

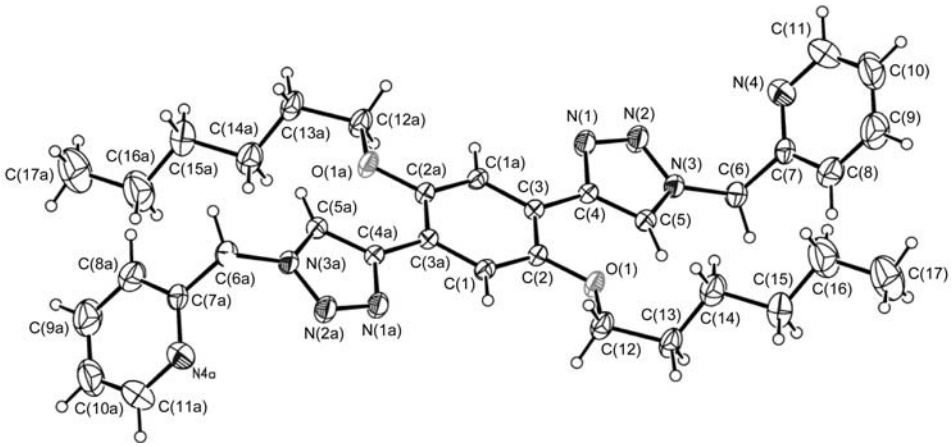


Figure 4 Crystal structure of **5a**.

Experimental

Reagents and instruments

^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian MECUYRVX300 spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal reference. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. FT-IR experiment was carried out on a NICOLET 170SX FT-IR spectrometer with KBr pellets. Mass spectrometry was performed on a Finnigan Trance Mass spectrometer. The determination of crystal structure was performed on a Bruker Smart APEX II CCD detector using graphite monochromated Mo Kα radiation (λ= 0.71073 Å). All the chemicals and reagents employed in the experiments were commercial available and used without further purification.

General methods for ligand synthesis

The organic azides and all the bis-alkyls were synthesized according to the published methods.[13,14] The ligands were synthesized according to Ref. 5 (different solvent system was used for different starting materials indicated in Schemes 1—3): the alkyne (1.0 equiv.) was put into the flask with 30 mL of mixed solvent, then the fresh generated sodium ascorbate aqueous solution (10 mol%, 5 mL) was added, followed by $CuSO_4$•$5H_2O$ aqueous solution (2 mol%, 5 mL). The organic azide (1.1 equiv. for each alkyne group in each molecule) was added finally. The mixture was stirred under 50 ℃ for 12 h, then cooled to room temperature, poured into 100 mL of ice cooled water. After 1 h, it was extracted with CH_2Cl_2, and the organic layer was collected and dried over $MgSO_4$. After filtration, the concentrated crude product was purified by chromotography (Table 1) and further purified by recrystallization.

Caution: The organic azides and sodium azide are potentially explosive hazards, they should be stored in a refrigerator and handled with great care!

Characterization data for all compounds

Compound 3a ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.61 (d, J=3.9 Hz, 1H), 7.94 (s, 1H), 7.83 (d, J=7.5 Hz, 2H), 7.70 (t, J=7.5 Hz, 1H), 7.41 (t, J=7.5 Hz, 2H), 7.34—7.25 (m, 3H), 5.71 (s, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 55.9, 120.5, 122.6, 123.7, 125.9, 128.4, 129.0, 130.7, 137.6, 148.4, 145.0, 154.7; IR (KBr) v: 3118, 3092, 3044, 3008, 2982, 2942, 2913, 1591, 1478, 1433, 1357, 1331, 1290, 1222, 1195, 1150, 1076, 1050, 1076, 1050, 994, 970, 912, 841, 816, 770, 749, 719, 695, 588, 560, 512, 475 cm^{-1}; MS (EI) m/z: 237.2 (M^+). Anal. calcd for $C_{14}H_{12}N_4$: C 71.17, H 5.12, N 23.71; found C 71.55, H 4.81, N 23.33.

Compound 3b ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.66 (s, 1H), 8.64 (d, J=4.5 Hz, 1H), 7.80 (d, J=7.2 Hz), 7.71 (s, 1H), 7.64 (d, J=7.8 Hz, 1H), 7.41 (t, J= 7.2 Hz, 2H), 7.31 (t, J=6.9 Hz, 2H), 5.62 (s, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 51.6, 119.4, 125.7, 128.4, 128.8, 130.2, 135.6, 148.6, 149.0, 150.2; IR (KBr) v: 3128, 3094, 3058, 3030, 2985, 2948, 1597, 1576, 1481, 1463, 1425, 1355, 1336, 1223, 1189, 1136, 1074, 1048, 1031, 919, 814, 759, 700, 592, 560, 512 cm^{-1}; MS (EI) m/z: 237.2 (M^+). Anal. calcd for $C_{14}H_{12}N_4$: C 71.17, H 5.12, N 23.71; found C 71.28, H 5.30, N 24.07.

Compound 3c ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.65 (s, 2H), 7.83 (d, J=7.2 Hz, 2H), 7.76 (s, 1H), 7.43 (t, J=6.9 Hz, 2H), 7.37 (t, J=6.9 Hz, 1H), 7.18 (s, 2H), 5.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 52.0, 119.4, 121.4, 125.0, 127.8, 128.2, 129.4, 143.0, 147.8, 149.8; IR (KBr) v: 3116, 3089, 3032, 2944, 1602, 1561, 1483, 1464, 1438, 1417, 1350, 1224, 1189, 1077, 1047, 973, 908, 859, 822, 765, 718, 692, 583, 508, 486 cm^{-1}; MS (EI) m/z: 237.2 (M^+). Anal. calcd for $C_{14}H_{12}N_4$: C 71.17, H 5.12, N 23.71; found C 71.23, H 5.16, N 24.03.

Compound 4a ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.59 (d, J=3.9 Hz, 2H), 7.93 (s, 2H), 7.85 (s, 4H), 7.67 (t, J_1=7.5 Hz, J_2=8.1 Hz, 2H), 7.27—7.21 (m, 4H), 5.67 (s, 4H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 55.3, 122.9, 124.0, 126.3, 130.8, 138.1, 146.9, 150.2, 155.6; IR (KBr) v: 3147, 3094, 3050, 3005, 2921, 2851, 1591, 1569, 1497, 1461, 1434, 1387, 1361, 1316, 1294, 1263, 1236, 1204, 1171, 1150, 1075, 1047, 1002, 938, 874, 845, 797, 715, 598 cm^{-1}; MS (EI) m/z: 394.2 (M^+). Anal. calcd for $C_{22}H_{18}N_8$: C 66.99, H 4.60, N 28.41;

found C 67.26, H 4.46, N 28.21.

Compound 4b ^{1}H NMR (DMSO, 300 MHz) δ: 8.72 (s, 2H), 8.67 (s, 2H), 8.57 (d, J=3.9 Hz, 2H), 7.92 (s, 4H), 7.78 (d, J=7.8 Hz, 2H), 7.46—7.41 (m, 2H), 5.73 (s, 4H); IR (KBr) v: 3128, 3095, 3013, 2951, 2928, 2859, 1639, 1598, 1575, 1479, 1453, 1433, 1358, 1316, 1256, 1220, 1150, 1075, 1047, 996, 975, 891, 832, 806, 751, 722, 601, 565 cm^{-1}; MS (EI) m/z: 394.8 (M^+). Anal. calcd for $C_{22}H_{18}N_8$: C 66.99, H 4.60, N 28.41; found C 67.24, H 4.11, N 28.68.

Compound 4c ^{1}H NMR (DMSO, 300 MHz) δ: 8.65 (d, J=3.0 Hz, 4H), 7.90 (s, 4H), 7.79 (s, 2H), 7.17 (d, J=5.1 Hz, 4H), 5.73 (s, 4H); IR (KBr) v: 3129, 3077, 3021, 2927, 2853, 1592, 1460, 1435, 1363, 1306, 1227, 1193, 1143, 1075, 1047, 989, 900, 851, 827, 798, 753, 720, 605, 557, 452 cm^{-1}; MS (EI) m/z: 394.4 (M^+). Anal. calcd for $C_{22}H_{18}N_8$: C 66.99, H 4.60, N 28.41; found C 66.78, H 4.42, N 28.31.

Note: For compounds **4b** and **4c**, due to their low solubility in DMSO-d_6, it was unable to obtain clear signals when trying to obtain the ^{13}C NMR spectra of these two samples. And the solubility of these three compounds was very low for their rigid structure, for the rich containing of nitrogen atoms, they might be seriously attached to the silica, so the separation yield was relatively low.

Compound 5a ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.62 (d, J=4.5 Hz, 2H), 8.24 (s, 2H), 7.99 (s, 2H), 7.68 (t, 2H), 7.29—7.25 (m, 2H), 7.16 (d J=7.8 Hz, 2H), 5.73 (s, 4H), 4.15 (t, 4H), 1.87—1.78 (m, 4H), 1.43—1.40 (m, 4H), 1.30—1.28 (m, 8H), 0.88 (t, J=6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 13.9, 22.5, 25.7, 29.3, 31.4, 55.5, 68.8, 110.5, 119.1, 122.01, 123.0, 123.2, 123.8, 137.2, 143.6, 149.3, 149.6, 154.8; IR (KBr) v: 3147, 3094, 3050, 3005, 2921, 2851, 1591, 1569, 1497, 1461, 1434, 1387, 1361, 1316, 1294, 1263, 1236, 1204, 1171, 1150, 1075, 1047, 1002, 938, 874, 845, 797, 715, 598 cm^{-1}; MS (EI) m/z: 594.8 (M^+). Anal. calcd for $C_{34}H_{42}N_8O_2$: C 68.66, H 7.12, N 18.84; found C 68.87, H 6.93, N 18.89.

Compound 5b ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.63 (d, J=4.5 Hz, 2H), 8.26 (s, 2H), 7.99 (s, 2H), 7.71 (t, J=7.5 Hz, 2H), 7.31—7.26 (m, 2H), 7.20 (d, J=7.8 Hz), 5.76 (s, 4H), 4.15 (t, J=6.6 Hz, 4H), 1.85—1.78 (m, 8H), 1.42—1.25 (m, 32H), 0.88 (t, 6H, m, the proton signal from alkyl chain, 46H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 14.4, 22.9, 26.4, 29.6, 29.9, 32.1, 55.8, 69.1, 10.9, 119.4, 122.4, 123.5, 124.2, 137.5, 143.9, 149.7, 149.9, 155.2; IR (KBr) v: 3162, 3083, 3055, 3016, 2923, 2848, 1592, 1569, 1500, 1467, 1432, 1381, 1342, 1381, 1342, 1237, 1202, 1067, 1038, 1002, 880, 830, 756, 721, 563 cm^{-1}; MS (EI) m/z: 763.3 (M^+). Anal. calcd for $C_{46}H_{66}N_8O_2$: C 72.40, H 8.72, N 14.68; found C 72.53, H 9.14, N 14.18.

Compound 6a ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 8.62 (d, J=4.4 Hz, 2H), 8.52 (s, 2H), 7.96—7.94 (m, 4H), 7.66 (t, J=6.0 Hz, 2H), 7.37 (d, J=8.8 Hz, 2H), 7.28—7.22 (m, 4H), 5.74 (s, 4H), 4.22 (t, J=5.4 Hz, 2H), 1.84—1.81 (m, 2H), 1.34—1.22 (m, 6H), 0.83 (t, J=5.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 13.9, 22.4, 26.8, 28.8, 31.4, 43.1, 55.6, 117.8, 119.4, 121.6, 122.3, 123.0, 123.3, 123.8, 137.3, 140.6, 149.0, 149.7, 154.6; IR (KBr) v: 3128, 3095, 3013, 2951, 2928, 2859, 1639, 1598, 1575, 1479, 1453, 1433, 1358, 1316, 1256, 1220, 1150, 1075, 1047, 996, 975, 891, 832, 806, 751, 722, 601, 565 cm^{-1}; MS (EI) m/z: 567.7 (M^+). Anal. calcd for $C_{34}H_{33}N_9$: C 71.93, H 5.86, N 22.21; found C 71.61, H 5.48, N 22.13.

Compound 6b ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.66 (d, J=4.5 Hz, 2H), 8.56 (s, 2H), 7.98 (t, J=6.9 Hz, 4H), 7.72 (t, J=6.3 Hz, 2H), 7.44 (d, J=8.4 Hz, 2H), 7.31—7.26 (m, 4H), 5.75 (s, 4H), 4.31 (t, J=6.9 Hz, 2H), 1.89 (m, 2H), 1.40—0.84 (m, 18H), 0.86 (t, J=6.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 12.3, 22.8, 27.4, 29.1, 29.5, 29.7, 32.0, 43.4, 55.9, 109.3, 118.0, 119.6, 121.9, 122.6, 123.2, 123.6, 124.1, 137.5, 140.9, 149.3, 149.9, 154.8; IR (KBr) v: 3139, 3094, 3055, 3013, 2923, 2851, 1648, 1631, 1614, 1593, 1479, 1438, 1354, 1318, 1252, 1220, 1148, 1078, 1049, 994, 887, 847, 804, 757, 721, 563, 477 cm^{-1}; MS (EI) m/z: 651.9 (M^+). Anal. calcd for $C_{40}H_{45}N_9$: C 73.70, H 6.96, N 19.34; found C 74.15, H 7.06, N 19.56.

Compound 7a ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.64 (d, J=5.2 Hz, 2H), 8.01 (s, 2H), 7.90 (s, 2H), 7.77—7.69 (m, 6H), 7.31—7.27 (m, 4H), 5.73 (s, 4H), 2.06—2.01 (m, 4H), 1.22—0.96 (m, 12H), 0.71 (t, J=6.9 Hz, 6H), 0.60 (m, 4H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 14.2, 22.8, 24.0, 29.9, 31.8, 40.8, 55.7, 56.0, 119.97, 120.2, 120.3, 120.4, 122.6, 123.7, 124.8, 130.0, 137.7, 141.1, 149.0, 150.0, 152.0, 154.7; IR (KBr) v: 3129, 3077, 3021, 2927, 2853, 1592, 1460, 1435, 1363, 1306, 1227, 1193, 1143, 1075, 1047, 989, 900, 851, 827, 798, 753, 720, 605, 557, 452 cm^{-1}; MS (EI) m/z: 650.9 (M^+). Anal. calcd for $C_{41}H_{46}N_8$: C 75.66, H 7.12, N 17.22; found C 75.81, H 6.79, N 17.53.

Compound 7b ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.62 (d, J=6.0 Hz, 2H), 7.99 (s, 2H), 7.88 (s, 2H), 7.73—7.68 (m, 6H), 7.29—7.25 (m, 4H), 5.72 (s, 4H), 2.03—1.99 (m, 4H), 1.24—0.98 (m, 36H), 0.84 (t, J=6.6 Hz, 6H), 0.60 (m, 4H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 14.3, 22.8, 27.4, 29.1, 29.5, 29.7, 32.0, 43.4, 55.9, 109.3, 118.0, 119.6, 121.9, 122.6, 123.2, 123.6, 124.1, 137.5, 140.1, 149.3, 149.9, 154.8; IR (KBr) v: 3162, 3083, 3055, 3016, 2923, 2848, 1592, 1570, 1500, 1467, 1432, 1381, 1342, 1237, 1202, 1067, 1038, 1002, 880, 830, 756, 721, 563 cm^{-1}; MS (EI) m/z: 819.8 (M^+). Anal. calcd for $C_{53}H_{30}N_8$: C 77.71, H 8.61, N 13.68; found C 77.63, H 8.60, N 13.14.

Compound 8 ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 8.59 (d, J=4.5 Hz, 3H), 7.86 (s, 3H), 7.69 (t, J=9.0 Hz, 6H), 7.28—7.20 (m, 9H), 7.14 (d, J=8.1 Hz, 6H), 5.68 (s, 6H); ^{13}C NMR ($CDCl_3$, 300 MHz) δ: 55.9, 120.0, 122.6, 123.7, 124.6, 125.6, 127.0, 137.6, 147.4, 148.1, 150.0, 154.8; IR (KBr) v: 3136, 3100, 3049, 3004, 2946, 1609, 1558, 1494, 1458, 1434, 1358, 1322, 1282, 1225, 1187, 1077, 1049, 974, 837, 755, 723, 598, 543 cm^{-1}. Anal.

calcd for $C_{44}H_{33}N_{13}$: C 70.08, H 4.62, N 25.30; found C 69.72, H 4.76, N 25.01.

Complex Cu(II)-3a and Cu(II)-3c The complex Cu(II)-**3a** was obtained from a layered method by carefully adding methanol solution of $CuCl_2 \cdot 2H_2O$ onto a CH_2Cl_2 solution of **3a**. Blue crystals. IR (KBr) *v*: 3118, 3094, 3068, 3034, 2996, 1639, 1607, 1574, 1485, 1438, 1356, 1316, 1227, 1194, 1156, 1073, 1056, 1025, 972, 831, 764, 720, 697, 605, 516, 477 cm^{-1}. Anal. calcd for $C_{28}H_{24}Cl_2CuN_8$: C 55.40, H 3.99, N 18.46; found C 55.53, H 4.38, N 18.35.

Complex Cu (II)-**3c** was synthesized as in Cu(II)-**3c**. Blue crystals. IR (KBr) *v*: 3126, 3085, 3030, 2921, 1618, 1518, 1463, 1429, 1358, 1319, 1228, 1191, 1146, 1074, 1047, 967, 909, 858, 810, 767, 720, 694, 611, 551, 490, 461 cm^{-1}. Anal. calcd for $C_{84}H_{72}Cl_6Cu_3N_{24}$: C 55.40, H 3.99, N 18.46; found C 54.80, H 3.99, N 18.49.

Complex Co(II)-3a The product had been grown by a layered method, in which the layered $CoCl_2$ acetone solution was onto an acetone solution of **3a**. Red-purple crystals. IR (KBr) *v*: 3135, 3057, 2983, 2935, 1654, 1606, 1574, 1481, 1437, 1359, 1322, 1234, 1201, 1161, 1086, 1065, 1020, 975, 831, 766, 719, 697, 663, 611, 511, 479 cm^{-1}. Anal. calcd for $C_{28}H_{24}N_8Cl_2Co$: C 55.83, H 4.02, N 18.60; found C 55.71, H 3.92, N 18.27.

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16 Crystallographic data for Cu(II)-**3c**, Co(II)-**3a** and **5a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary materials with the number CCDC 777713, 759810 and 759811. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

17 Crowley, J. D.; Bandeen, P. H.; Hanton, L. R. *Polyhedron* **2010**, *29*, 70. When we prepared this manuscript, the complex Cu(II)-**3a** had been reported in this reference. But in their work the Cu—N(2) distance was 2.693(2) Å and 2.672(2) Å, repectively, which has a little difference from the data in this work.

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