Synthesis of Novel Molecular Clips via Click Chemistry Based on Diethoxy carbonyl Glycoluril

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Abstract: A novel class of molecular clips based on diethoxycarbonyl glycoluril was synthesized via click chemistry. Seven different arylacetylenes were used in this research, and all reaction products gave satisfying ^{1}H NMR, ^{13}C NMR, HRMS, and IR spectra. The structure and conformation of **7a** were further confirmed by single-crystal X-ray diffraction. A primary study on the metal-ion binding ability of **7f** showed that its fluorescence was obviously quenched by Fe^{3+}, Ag^+, and Cu^{2+} among metal ions examined.

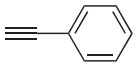
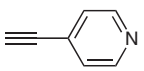
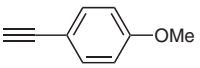
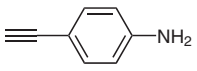
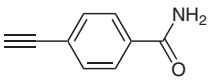
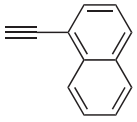
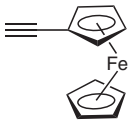
Key words: clip receptor, diethoxycarbonyl glycoluril, molecular recognition, 1,2,3-triazole, fluorescence

Natural receptors play fundamental roles in molecular recognition, catalysis, and transport processes. Inspired by nature, artificial receptors have been developed to mimic these functions.[1] The rigid concave shape of glycoluril makes it a versatile building block to construct various supramolecular objects, such as molecular capsules,[2] molecular clips,[3] and cucurbit[*n*]uril family.[4] Especially glycoluril-based clips with a preorganized cleft and rigid aromatic arms have been proved to be effective receptors for hydroxybenzene derivatives,[5] metal ions,[6] and anions.[7] In order to expand the range of possible guest structures, we would like to introduce new binding sites and flexible side arms in the glycoluril-based clips.[1a]

'Click chemistry' developed by Meldal[8] and Sharpless[9] for constructing 1,2,3-triazole compounds has found growing applications in bioconjugation, drug discovery, materials and supramolecular chemistry.[10] Besides the advantages of its reliability, regioselectivity, and compatibility with reaction conditions, the unique structural features of the 1,2,3-triazole ring–free electron pairs on nitrogen, polarized proton, large dipole moment, and aromatic stability, render it active participation in hydrogen bonding, metal–lone pair bonding, dipole–dipole and π–π stacking interactions.[10e,11] Recently, some triazole-based receptors with interesting binding properties have been reported, such as cyclodextrins,[12] calix[4]arenes,[13] dendrimers,[14] macrocycles,[15] foldmers,[16] and bile acids.[17] These results demonstrate that 1,2,3-triazole ring can play an important role in molecular recognition. However, to our knowledge, the potential application of 1,2,3-triazole ring in glycoluril-based clips has not yet been explored.

In connection with our ongoing program on the synthesis of novel molecular clips and the interesting structural features of the 1,2,3-triazole ring, we were interested in exploring this versatile reaction on diethoxycarbonyl glycoluril to synthesize novel molecular clips with 1,2,3-triazole rings in flexible side arms.

Table 1 Synthesis of **7a–g** from Arylacetylenes

Entry	$R^2C{\equiv}CH$	Product	Yield (%)[a]
1		**7a**	80
2		**7b**	70
3		**7c**	78
4		**7d**	74
5		**7e**	75
6		**7f**	82
7		**7g**	82

[a] Isolated yield.

The synthetic route used to obtain clips **7a–g** is shown in Scheme 1. Diethoxycarbonyl glycoluril **3**, which has a high degree of organic solubility unlike most other glycolurils, was synthesized according to the literature procedure[18] and used for these studies. As we previously reported,[19] compound **4** could be smoothly prepared by treatment of **3** with ethanolamine in the presence of formaldehyde in MeOH. Tosylation of the hydroxyl group of **4** with TsCl afforded compound **5** in 61% yield.[20] The tosylate **5** was reacted with sodium azide in DMF to give compound **6** in 88% yield.[21] Treatment of azide **6** with a number of arylacetylenes in *t*-BuOH–H_2O (1:1) in the presence of $CuSO_4$ and ascorbic acid (click reaction)[9]

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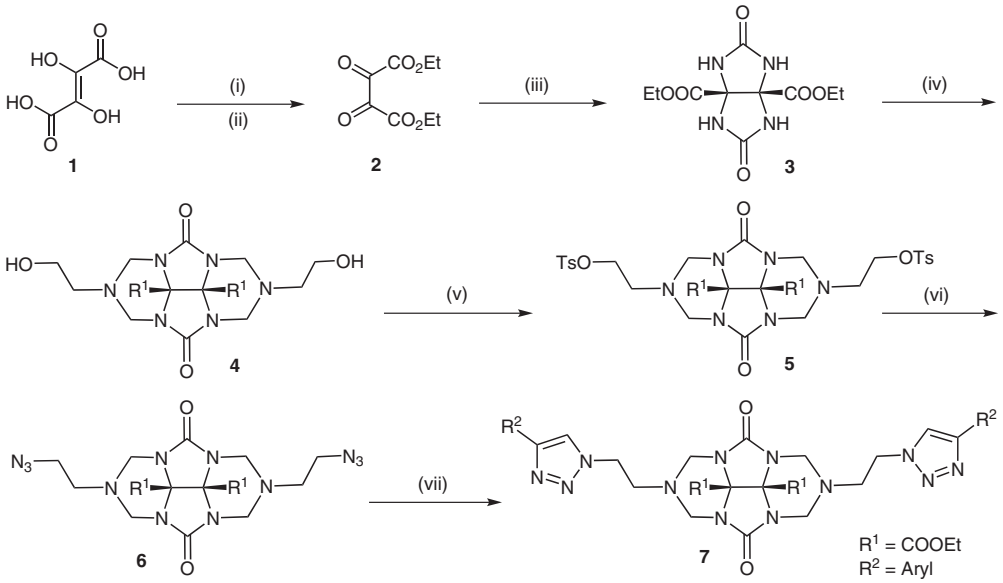

Scheme 1 *Reagents and conditions*: (i) AcOH, Br_2, H_2O; (ii) EtOH, HCl(g), 0 °C; (iii) PhH, H_2NCONH_2, TFA, reflux; (iv) $NH_2CH_2CH_2OH$, 37% aq HCHO, MeOH, reflux; (v) TsCl, Et_3N, CH_2Cl_2, r.t., 61%; (vi) NaN_3, DMF, 60 °C, 88%; (vii) $R^2C{\equiv}CH$, $CuSO_4$, ascorbate acid, *t*-BuOH–H_2O, r.t., 70–82%.

gave the expected molecular clips **7a–g** in 70–82% yield (Table 1).

Taking into consideration that the nature of the substituents in arylacetylene could affect the binding properties, a variety of arylacetylenes were used in this research. In addition to phenylacetylene, we had synthesized 4-ethynylpyridine[22] and three *para*-substituted phenylacetylenes[23] with electron-donating or -withdrawing groups. To further enlarge the scope of the clip receptor as a fluorescent or electrochemical sensor, we attached 1-naphthalenyl group[24] and ferrocenyl group[25] to the triazole units, which may allow us to monitor the binding ability of the 1,2,3-triazole ring by fluorescence or cyclic voltammetry (CV). All reaction products gave satisfactory ^{1}H NMR, ^{13}C NMR, HRMS, and IR data.[26] In addition, the structure and conformation of compound **7a** were further elucidated by single-crystal X-ray diffraction,[27] as shown in Figure 1. Compound **7a** has a well-defined geometry due to the rigidity that the fused rings confer on the molecule. It is built up from four fused rings, namely two nearly planar imidazole five-membered rings and two nonplanar triazine six-membered rings. Both six-membered rings have chair conformations. The distance between two carbonyl oxygen atoms (O_1–O_2) of the glycoluril moiety is 5.299 Å. The distance between the centers of two trizole rings is 6.388 Å, and the dihedral angle between two trizole rings is 9.00°. The flexible spacer connecting the glycoluril cavity and 1,2,3-triazole ring can contribute to the conformational flexibility of this host, allowing it to adopt the most favorable conformation for guest complexation.

Because fluorescent chemosensors have advantages of high selectivity, sensitivity, and simplicity in molecular recognition,[28] we first chose **7f** to screen its metal-ion binding ability. The fluorescence spectrum of **7f** (10 μM)

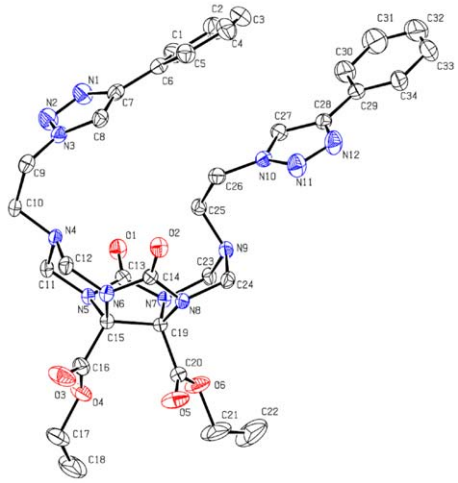

Figure 1 X-ray crystal structure of compound **7a**; hydrogen atoms are omitted for clarity

in THF–MeOH (v/v, 50:1) was found to exhibit maximum emission at 350 nm (excitation at 301 nm). Seventeen metal ions were screened by comparing the fluorescence intensities of the solutions before and after adding 10 equivalents metal ions as their chloride or nitrate salts: K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Al^{3+}, Sn^{2+}, and Pb^{2+}. The results are shown in Figure 2.

We found that the fluorescence of **7f** (10 μM) was obviously quenched by Fe^{3+}, Ag^+, and Cu^{2+} ions. Comparing these results with what we previously reported,[6] we speculated that Fe^{3+} was bound in the cavity of the clip, the fluorescent aromatic units of side arms probably behaved as PET donors whereas the bound Fe^{3+} as electron acceptors, which led to a severe fluorescence quenching.[29] However, complexation of Ag^+ and Cu^{2+} ions requires the

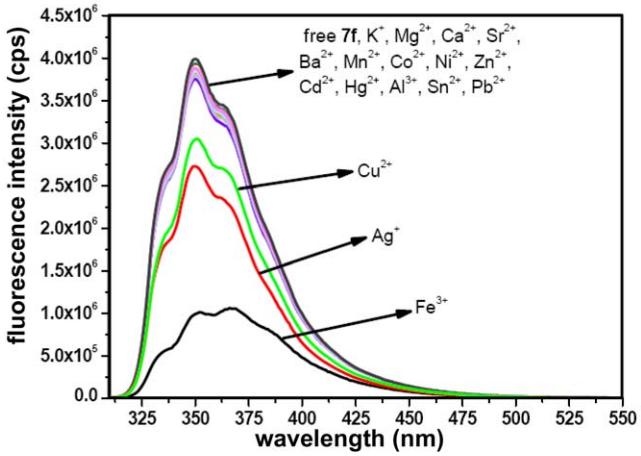

Figure 2 Fluorescence emission spectra of **7f** (10 μM) in THF–MeOH (v/v, 50:1) in the presence of 10 equiv various metal ions (excitation at 301 nm)

coordination of the two triazole groups of **7f**. This was supported by silver(I) ion induced chemical shift of **7f** changes in the ^{1}H NMR spectra (see Figure 3). In the presence of 5.0 equivalents of Ag^+ ions, chemical shifts of protons H_a–H_d downfield shifted by 0.02, 0.06, 0.06, and 0.07 ppm, respectively. The peak of H_e on the triazole group was downfield shifted by 0.19 ppm, but the peaks of H_f and H_g were upfield shifted by 0.31 and 0.09 ppm. These results suggest that the two triazole groups are involved in the complexation with Ag^+.

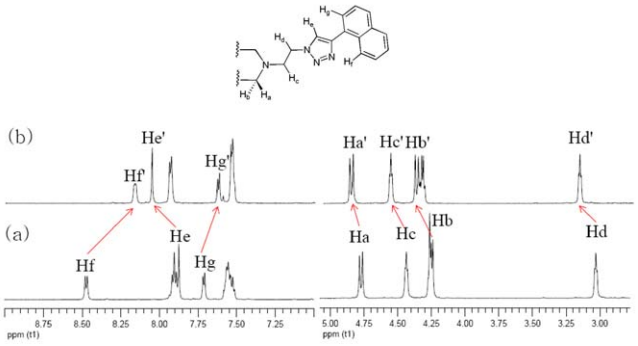

Figure 3 (a) ^{1}H NMR (600 MHz, CD_3CN) spectra of **7f** (5 mM); (b) in the presence of 5.0 equiv of silver nitrate

The fluorescence spectra of **7f** (10 μM) at various concentrations of Ag^+ ions are depicted in Figure 4; as can be seen, no shift in the fluorescence maximum was observed. However, the fluorescence intensities of **7f** gradually decreased as the concentration of Ag^+ increased from 10 to 240 μM. In the Job plot (see inset of Figure 4),[30] a maximum fluorescence change was observed when the molar fraction of **7f** vs Ag^+ was 0.5, indicative of a 1:1 complex. Similar fluorescence titration behavior and a 1:1 binding stoichiometry was also observed in the cases of **7f** with Cu^{2+} and Fe^{3+} ions, respectively (see supporting information for details).

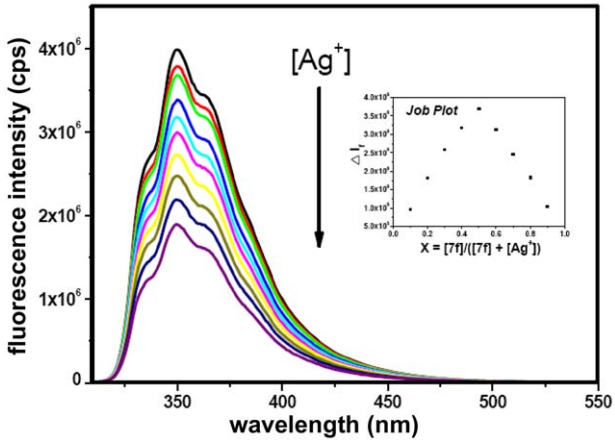

Figure 4 Fluorescence emission spectra (excitation at 301 nm) of **7f** (1.0×10^{-5} M) in THF–MeOH (50:1, v/v) in the presence of $AgNO_3$; concentration of Ag^+: 0, 1.0, 2.0, 4.0, 6.0, 8.0, 10.0, 14.0, 18.0, and 24.0×10^{-5} M

In summary, we have synthesized a novel class of molecular clips based on diethoxycarbonyl glycoluril via click chemistry. The primary study on the metal ion binding ability of **7f** shows that its fluorescence was obviously quenched by Fe^{3+}, Ag^+, and Cu^{2+} among seventeen metal ions examined. Further studies on the quenching mechanism and other molecular clips' binding behavior are under way in our laboratory.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

Acknowledgment

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(20) Compound **5**: IR (KBr): 2984, 1721, 1598, 1415, 1358, 1176, 907, 817, 663, 554 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.4 Hz, 4 H), 7.35 (d, *J* = 8.4 Hz, 4 H), 4.73 (d, *J* = 14.4 Hz, 4 H), 4.30–4.25 (m, 8 H), 4.04 (t, *J* = 5.2 Hz, 4 H), 2.90 (t, *J* = 5.2 Hz, 4 H), 2.48 (s, 6 H), 1.30 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 164.8, 158.3, 144.8, 132.5, 129.7, 127.7, 75.8, 67.2, 63.3, 59.7, 49.7, 21.4, 13.6. ESI-MS: *m/z* = 765.0 $[M + H]^+$.
(21) Compound **6**: IR (KBr): 2989, 2100, 1767, 1709, 1407, 1276, 899, 725 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.88 (d, *J* = 14.0 Hz, 4 H), 4.36 (d, *J* = 14.0 Hz, 4 H), 4.30 (q, *J* = 7.2 Hz, 4 H), 3.36 (t, *J* = 5.6 Hz, 4 H), 2.90 (t, *J* = 5.6 Hz, 6 H), 1.32 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 158.4, 76.0, 63.4, 59.9, 50.4, 48.6, 13.8. ESI-MS: *m/z* = 506.2 $[M]^+$.
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(25) Polin, J.; Schottenberger, H. *Org. Synth.* **1996**, *73*, 262.
(26) **General Procedure for the Synthesis of Compound 7**
The azide **6** (0.20 mmol) and arylacetylene (0.40 mmol) were suspended in 1:1 mixture of H_2O and *t*-BuOH (10 mL). Ascorbate acid (0.020 mmol, 20 μL of freshly prepared 1.0 M solution in H_2O, 10 mol%) was added, followed by copper(II) sulfate pentahydrate (0.010 mmol, 100 μL of 0.10 M solution in H_2O, 5.0 mol%). The heterogeneous mixture was stirred vigorously for 24 h under Ar protection. After total consumption of the starting material (determination by TLC), the solvent was removed in vacuo, and the residue was isolated by column chromatography on SiO_2 to get the pure product **7**.
Compound **7a**: IR (KBr): 3244, 2985, 1705, 1444, 1282, 1047, 767, 697 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 7.6 Hz, 4 H), 7.60 (s, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 7.35 (t, *J* = 7.6 Hz, 2 H), 4.82 (d, *J* = 13.6 Hz, 4 H), 4.36 (t, *J* = 6.0 Hz, 4 H), 4.28 (q, *J* = 7.2 Hz, 4 H), 4.19 (d, *J* = 13.6 Hz, 4 H), 2.93 (t, *J* = 6.0 Hz, 4 H), 1.30 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 158.6, 147.3, 130.6, 128.9, 128.1, 125.6, 120.3, 76.0, 63.5, 60.0, 50.1, 47.0, 13.8. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{34}H_{38}N_{12}NaO_6$: 733.2929; found: 733.2898.
Compound **7b**: IR (KBr): 3423, 3137, 2988, 1766, 1730, 1707, 1612, 1411, 1286, 1234, 1045, 907, 718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.68 (d, *J* = 5.6 Hz, 4 H), 7.88 (s, 2 H), 7.77 (d, *J* = 5.6 Hz, 4 H), 4.81 (d, *J* = 13.6 Hz, 4 H), 4.45 (t, *J* = 5.2 Hz, 4 H), 4.31–4.22 (m, 8 H), 3.03 (t, *J* = 5.2 Hz, 4 H), 1.31 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.7, 158.5, 150.3, 144.9, 137.9, 122.0, 119.8, 75.9, 63.6, 59.9, 50.1, 47.6, 13.8. ESI-HRMS: *m/z* $[M+Na]^+$ calcd for $C_{32}H_{36}N_{14}NaO_6$: 735.2834; found: 735.2814.
Compound **7c**: IR (KBr): 3447, 3134, 2939, 2840, 1760, 1718, 1459, 1299, 1248, 1231, 1027, 825, 717 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.4 Hz, 4 H), 7.50 (s, 2 H), 6.97 (d, *J* = 8.4 Hz, 4 H), 4.82 (d, *J* = 13.2 Hz, 4 H), 4.33–4.25 (m, 8 H), 4.18 (d, *J* = 13.2 Hz, 4 H), 3.80 (s, 6 H), 2.88 (t, *J* = 6.0 Hz, 4 H), 1.30 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 159.5, 158.5, 147.2, 126.9, 123.3, 119.5, 114.2, 76.0, 63.5, 60.0, 55.2, 50.1, 46.8, 13.8. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{36}H_{42}N_{12}NaO_8$: 793.3141; found: 793.3100.
Compound **7d**: IR (KBr): 3448, 3367, 2982, 2849, 1720, 1621, 1502, 1416, 1291, 1233, 1029, 906, 837, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, *J* = 8.0 Hz, 4 H), 7.48 (s, 2 H), 6.68 (d, *J* = 8.0 Hz, 4 H), 4.79 (d, *J* = 13.6 Hz, 4 H), 4.28–4.24 (m, 8 H), 4.12 (d, *J* = 13.6 Hz, 4 H), 3.90 (br s, 4 H), 2.87 (t, *J* = 6.0 Hz, 4 H), 1.27 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 158.5, 147.6, 146.7, 126.7, 120.6, 119.1, 115.1, 76.0, 63.5, 59.9, 50.0, 46.7, 13.8. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{34}H_{40}N_{14}NaO_6$: 763.3147; found: 763.3120.
Compound **7e**: IR (KBr): 3362, 3150, 2984, 2844, 1726, 1678, 1617, 1414, 1235, 1030, 982, 910, 858, 776, 713 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 8.50 (s, 2 H), 8.02 (s, 2 H), 7.98 (d, *J* = 8.0 Hz, 4 H), 7.91 (d, *J* = 8.0 Hz, 4 H), 7.42 (s, 2 H), 4.78 (d, *J* = 13.6 Hz, 4 H), 4.50 (t, *J* = 6.0 Hz, 4 H), 4.29–4.21 (m, 8 H), 3.01 (t, *J* = 6.0 Hz, 4 H), 1.21 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 167.5, 164.9, 158.3, 145.4, 133.4, 133.3, 128.3, 124.8, 122.5, 75.8, 63.5, 59.3, 49.6, 46.9, 13.7. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{36}H_{40}N_{14}NaO_8$: 819.3046; found: 819.2999.
Compound **7f**: IR (KBr): 3423, 3137, 2988, 1766, 1730, 1707, 1612, 1411, 1286, 1234, 1045, 907, 718 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.43 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 4 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.55–7.47 (m, 8 H), 4.82 (d, *J* = 13.6 Hz, 4 H), 4.34 (t, *J* = 6.0 Hz, 4 H), 4.27 (q, *J* = 7.2 Hz, 4 H), 4.20 (d, *J* = 13.6 Hz, 4 H), 2.95 (t, *J* = 6.0 Hz, 4 H), 1.28 (t, *J* = 7.2 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.8, 158.5, 146.5, 133.7, 130.7, 128.8, 128.3, 127.8, 127.1, 126.7, 126.0, 125.4, 125.3, 122.9, 75.9, 63.5, 60.0, 50.2, 47.1, 13.8. ESI-HRMS: *m/z* $[M + Na]^+$ calcd for $C_{42}H_{42}N_{12}NaO_6$: 833.3242; found: 833.3220.
Compound **7g**: IR (KBr): 3448, 3122, 2982, 1719, 1414, 1232, 1035, 906, 821, 712, 505, 488 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47 (s, 2 H), 4.81–4.78 (m, 8 H), 4.34–4.30 (m, 8 H), 4.27 (q, *J* = 7.2 Hz, 4 H), 4.20 (d, *J* = 13.2 Hz, 4 H), 4.10 (s, 10 H), 2.94 (t, *J* = 5.6 Hz, 4 H), 1.29 (t, *J* = 7.2

Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.9, 158.5, 146.4, 119.5, 76.0, 75.5, 69.6, 68.6, 66.5, 63.5, 60.0, 50.3, 47.1, 13.8. ESI-HRMS: *m/z* [M + Na]$^+$ calcd for $C_{42}H_{46}Fe_2N_{12}NaO_6$: 949.2273; found:949.2215.

(27) **Crystal Data for Compound 7a**
$C_{34}H_{38}N_{12}O_6$, *MW* = 710.78, triclinic, *a* = 10.0153 (5), *b* = 12.0495 (6), *c* = 16.3995 (8) Å, *a* = 102.658 (0)°, *b* = 103.272 (0)°, γ = 108.398 (0)°, *V* = 1734.28 (15) Å^3, *T* = 294 (2) K, space group *Z* = 4, *m*(MoKα) = 0.094 mm^{-1}, 15230 reflections measured, 6724 unique (*R*int = 0.0981) which were used in all calculations. The final wR_2 (F_2) was 0.1531. CCDC 699457 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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