Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

C$_3$-substituted cyclotriveratrylene derivative with 8-quinolinyl groups as a fluorescence-enhanced probe for the sensing of Cu^{2+} ions

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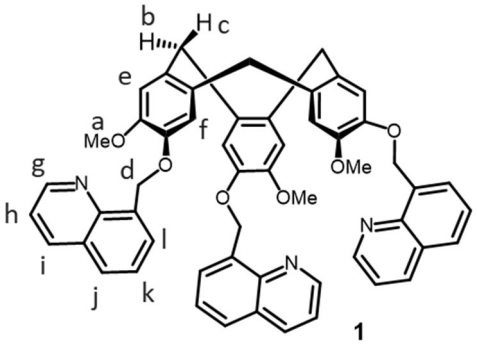
Experimental

1. ^{1}H, ^{13}C NMR, FTIR and HRMS data of the synthesized *C*$_3$-substituted CTV derivatives 1

The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Samples for the NMR spectra were examined in $CDCl_3$ solutions at 25.0 °C on a Varian 300MHz NMR spectrometer (XL-300). The ^{13}C NMR for *C*$_3$-substituted CTV **1** was recorded at 100 MHz in $CDCl_3$ solutions at 25.0 °C on a JEOL 400MHz NMR spectrometer (JNM-ECZ400S/L1). The chemical shifts are given in δ (ppm) relative to the deuterated solvents (^{13}C NMR) or to TMS (^{1}H NMR) as an internal standard. The IR spectra were run in KBr discs on a Shimazu FTIR-8600 spectrometer. High-resolution mass (HRMS) spectra (positive mode of EI mass) were recorded on a JEOL JMS-DX-303.

TRIS(8-QUINOLINYLMETHYL)CTG (1). white solid; mp 150-153 °C. ^{1}H NMR ($CDCl_3$): δ3.34 (d, 3Hb, H_{eq} of CH_2, J = 13.8 Hz), 3.54 (s, 9Ha, OMe), 4.60 (d, 3Hc, H_{ax} of CH_2, J = 13.8 Hz), 5.89 (d, 3Hd, OCH_2, J = 15.3 Hz), 5.97 (d, 3Hd, OCH_2, J = 15.3 Hz), 6.55 (s, 3He, C_6H_2), 6.89 (s, 3Hf, C_6H_2), 7.47 (dd, 3Hk, C_9H_6N, J = 8.4 and 4.2 Hz), 7.52 (dd, 3Hi, C_9H_6N, J = 8.4, and 6.9 Hz), 7.76 (dd, 3Hh, C_9H_6N, J = 8.4, and 1.2 Hz), 7.85 (dd, 3Hg, C_9H_6N, J = 6.9 and 1.2 Hz), 8.20 (dd, 3Hj, C_9H_6N, J = 8.4 and 1.8 Hz), 8.94 (dd, 3Hl, C_9H_6N, J = 4.2 and 1.8 Hz). ^{13}C NMR ($CDCl_3$): δ36.25 (CH_2), 55.83 (OMe), 67.07 (OCH_2), 113.01 (C_6H_2), 114.51 (C_6H_2), 121.16 (C_9H_6N), 126.71 (C_9H_6N), 127.98 (C_9H_6N), 127.06 (C_9H_6N), 127.96 (C_9H_6N), 131.50 (C_6H_2), 131.81 (C_6H_2), 135.30 (C_9H_6N), 136.32 (C_9H_6N), 145.38 (C_6H_2), 146.69 (C_6H_2), 147.79 (C_9H_6N), 149.35 (C_9H_6N). IR (KBr): 2929 (ν_{C-H}), 1606 ($\nu_{C=N-C}$), 1265 (ν_{C-O-C}) cm^{-1}. HRMS(FAB): m/z calcd. for $C_{54}H_{45}N_3O_6$ 831.3308, found [M+H] 832.3372.



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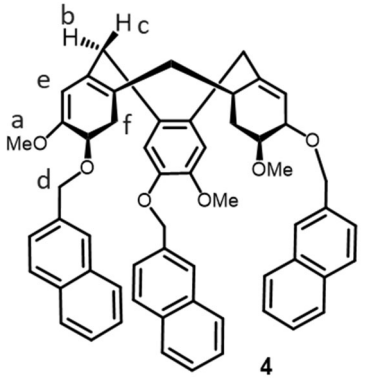
TRIS(2-NAPHTHYLMETHYL)CTG (4). orange solid; mp 140-142 °C. ^{1}H NMR ($CDCl_3$): δ3.32 (s, 9Ha, OMe), 3.40 (d, 3Hb, H_{eq} of CH_2, J = 13.8 Hz), 4.65 (d, 3Hc, H_{ax} of CH_2, J = 13.8 Hz), 5.23 (d, 3Hd, OCH_2, J = 13.2 Hz), 5.31 (d, 3Hd, OCH_2, J = 13.2 Hz), 6.51 (s, 3He, C_6H_2), 6.82 (s, 3Hf, C_6H_2), 7.45-7.52 (m, 9H, $C_{10}H_7$), 7.78-7.85 (m, 12H, $C_{10}H_7$). ^{13}C NMR ($CDCl_3$): δ36.70 (CH_2), 55.78 (OMe), 71.94 (OCH_2), 113.52 (C_6H_2), 116.05 (C_6H_2), 124.83 ($C_{10}H_7$), 125.54 ($C_{10}H_7$), 126.26 ($C_{10}H_7$), 126.53 ($C_{10}H_7$), 127.96 ($C_{10}H_7$), 128.16 ($C_{10}H_7$), 128.63 ($C_{10}H_7$), 131.69 (C_6H_2), 132.71 (C_6H_2), 133.24 ($C_{10}H_7$), 133.57 ($C_{10}H_7$), 135.39 ($C_{10}H_7$), 147.25 (C_6H_2), 148.52 (C_6H_2). IR (KBr): 2920 (ν_{C-H}), 1265 (ν_{C-O-C}) cm^{-1}. HRMS(FAB): m/z calcd. for $C_{57}H_{48}O_6$ 828.3451, found 828.3451.



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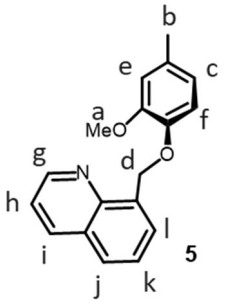
8-(2-METHOXY-4-METHYLPHENOXYMETHYL)QUINOLINE (5). white solid; mp 100-101 °C. ^{1}H NMR ($CDCl_3$): δ2.29 (s, 3Hb, CH_3), 3.93 (s, 3Ha, OMe), 5.93 (s, 2Hd, OCH_2), 6.61 (dd, 1Hc, C_6H_3, J = 8.1 and 1.5 Hz), 6.76 (d, 1He, C_6H_3, J = 1.5 Hz), 6.86 (d, 1Hf, C_6H_3, J = 8.1 Hz), 7.44 (dd, 1Hk, C_9H_6N, J = 8.4 and 4.2 Hz), 7.54 (dd, 1Hh, C_9H_6N, J = 8.4 and 7.2 Hz), 7.75 (d, 1Hi, C_9H_6N, J = 8.4 Hz), 7.94 (d, 1Hg, C_9H_6N, J = 7.2 Hz), 8.18 (dd, 1Hj, C_9H_6N, J = 8.4 and 1.5 Hz), 8.94 (dd, 1Hl, C_9H_6N, J = 4.2 and 1.5 Hz). ^{13}C NMR ($CDCl_3$): δ21.25 (CH_3), 56.24 (OMe), 67.39 (OCH_2), 113.15 (C_6H_3), 113.94 (C_6H_3), 121.11 (C_9H_6N), 121.32 (C_9H_6N), 126.77 (C_9H_6N), 127.19 (C_9H_6N), 127.26 (C_9H_6N), 128.21 (C_6H_3), 130.90 (C_6H_3). 135.77 (C_9H_6N), 136.51 (C_9H_6N), 145.79 (C_6H_3), 146.33 (C_6H_3), 149.47 (C_9H_6N), 149.65 (C_9H_6N). IR (KBr): 2920 (ν_{C-H}), 1516 ($\nu_{C=N-C}$), 1267 (ν_{C-O-C}) cm^{-1}. HRMS(FAB): m/z calcd. for $C_{18}H_{17}O_2$ 279.3417, found 279.1261.



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2. Time-dependent fluorescence intensity changes of C_3-substituted CTV derivative 1

The fluorescence emission spectra were recorded on a Shimazu RF-5300PC(S) luminescence spectrometer. The emission spectra from 340 to 770 nm were collected (every 1 nm).

The time-dependent experiment of the fluorescence intensity at 319 nm of C_3-substituted CTV **1** was performed in the presence of 1 equiv of Cu^{2+}. As shown in Fig. S1, the fluorescence intensity plateaued within ca. 30 min after the addition of Cu^{2+} ions.

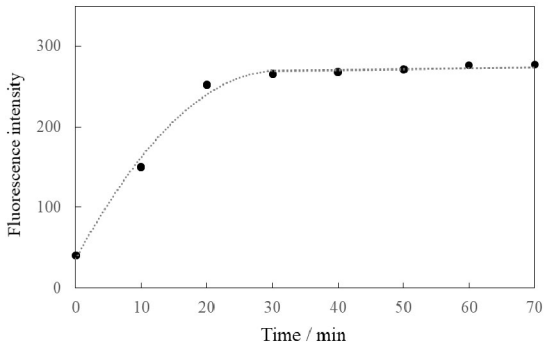
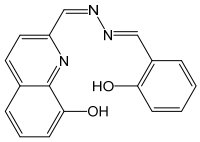
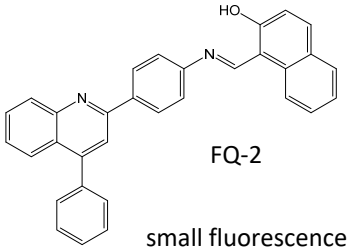
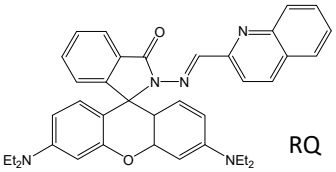
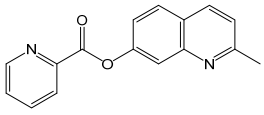
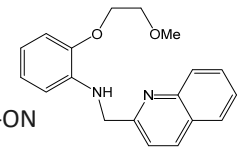
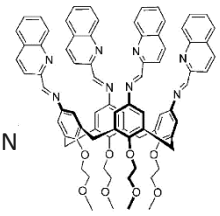


Fig. S1 Time-dependent fluorescence intensity changes of C_3-CTV derivatives **1** (10 μM) in the presence of 1 equiv of Cu^{2+} ion at 431 nm in CH_3CN (excitation wavelength: λ_{ex}=313 nm).

3. Comparison of quinoline-based fluorescence-enhanced probe for the Cu^{2+} ion

Table S1. Comparison of quinoline-based fluorescence-enhanced probes for the Cu^{2+} ion.

probe	solvent λ_{em} / λ_{em}	binding mode (reversibility)	mechanism	ref no.
 QH small fluorescence	DMSO:H_2O=1:1 352 nm / 623 nm	1 : 1	Cu^{2+}-chelating PET quenching	34
 FQ-2 small fluorescence	H_2O 380 nm / 490 nm	1 : 1 (reversible with EDTA)	Cu^{2+}-chelating PET quenching	35
 RQ small fluorescence	CH_3CN:H_2O=7:3 520 nm / ca. 585 nm	1 : 1	Cu^{2+}-promoted ring-opening of rhodamine spirolactam	34
 OFF-ON PQ very weak fluorescence	H_2O 390 nm / 502 nm		Cu^{2+}-promoted hydrolysis of picolinic moiety	36
 OFF-ON 1 very weak fluorescence	CH_3CN 315 nm / 412 nm	1 : 1	Cu^{2+}-chelating PET quenching	36
 OFF-ON 1 very weak fluorescence	CH_3CN 335 nm / 412 nm	1 : 1	Cu^{2+}-chelating PET quenching	36