Supporting Information

Conversion of Intramolecular Singlet Electron Transfer at Room Temperature into Triplet Energy Transfer at 77 K: Photoisomerization in Norbornadiene and Carbazole Labeled Poly(aryl ether) Dendrimers

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Experimental procedures for the synthesis of all dendritic compounds, including characterization data; Emission spectra and time-resolved fluorescence spectra of CZ-G*n*-NBD and CZ-G*n*-QC at room temperature (RT) and 77 K.

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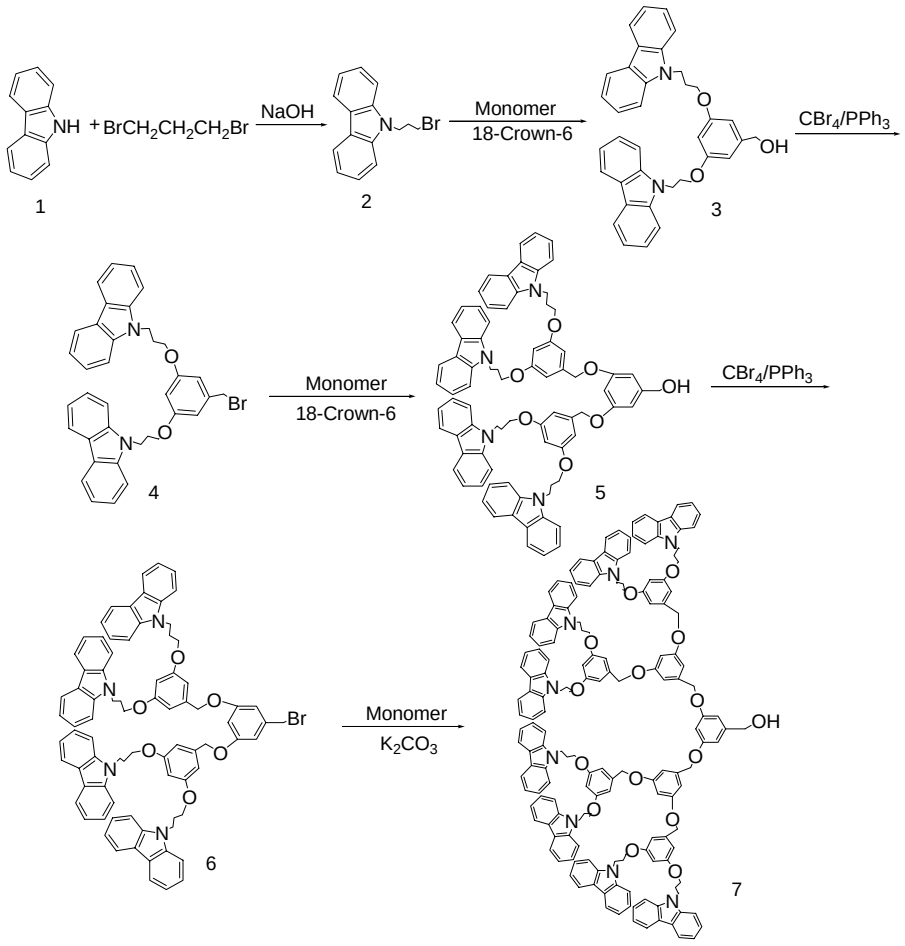
Synthesis of the CZ-Gn-OH and CZ-Gn-Br compounds. Dendritic benzyl alcohols and dendritic benzyl bromides were synthesized by Fréchet's method[1]. The reactions were carried out on scales of about 2 g. The mixture was washed with CH_2Cl_2 and water, the organic layer was dried, filtered, and evaporated under reduced pressure. The detailed procedures for synthesis and purification were described below

Scheme 1.



9-(3-bromopropyl)-carbazole (2) Carbazole (5.0 g), *N*,*N*,*N*-trimethylhexadecan-1-aminium bromide (0.12 g), 50% NaOH aqueous solution (20 g), and 1,3-dibromopropane (25 ml) were refluxed in THF (40 ml) for 48 h. The mixture was filtered, concentrated, washed with ethyl ether and water, dried and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether) to afford (2) as a white solid: yield 44%; IR υ 3051, 2943, 2873, 1594, 1483,

1325, 1260, 1233, 1191, 1153, 752, 725 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44-2.48 (m, 2H, -CH_2-), 3.39-3.43 (t, 2H, -NCH_2-), 4.50-4.55 (t, 2H, -CH_2Br), 7.29-8.13 (m, 8H, ArH).

CZ-G1-OH (3) It was prepared from (2) (2.20 equiv.), 3,5-dihydroxybenzyl alcohol (1.00 equiv.) as the monomer unit, potassium carbonate (2.20 equiv.) and 18-crown-6 (0.2 equiv.) in refluxing acetone under nitrogen with vigorous stirring for 48 h. The product was purified by column chromatography on silica gel (CH_2Cl_2/Et_2O 20/1) to give (3) as a white solid: yield 85%; IR υ 3340, 3048, 2876, 1595, 1485, 1452, 1346, 1327, 1289, 1166, 1070, 997, 982, 750, 720 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.32-2.36 (m, 4H, -CH_2-), 3.89-3.92 (m, 4H, -NCH_2-), 4.54-4.59 (m, 6H, -OCH_2- and -CH_2OH), 6.33-8.12 (m, 19H, ArH); MS: m/z 554 (M^+), calcd. m/z 554.68; Anal. calcd. for $C_{37}H_{34}N_2O_3$ C, 80.10; H 6.18; N 5.05; Found: C, 79.60; H 6.18; N 4.98.

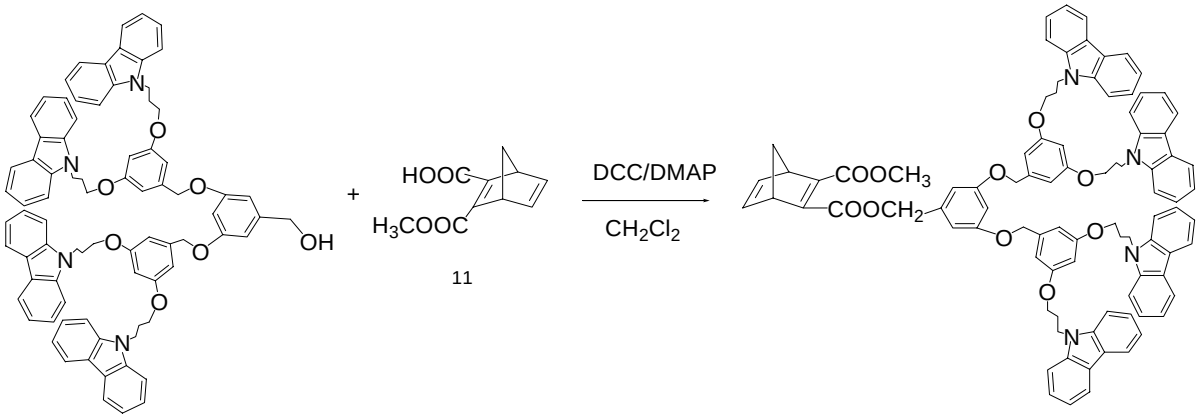
CZ-G1-Br (4) It was prepared from (3) (1.00 equiv.), requiring 2 × 1.25 equiv. of carbon tetrabromide (CBr_4) and triphenylphosphine (PPh_3), respectively, monitoring the reaction with TLC and the reaction is finished until the starting material disappeared. The product was purified by column chromatography eluting with petroleum ether/dichloromethane (1/1) to give (4) as a white solid: yield 86%; ^1H NMR ($CDCl_3$) δ 2.32-2.36 (m, 4H, -CH_2-), 3.87-3.91 (m, 4H, -NCH_2-), 4.39-4.58 (m, 6H, -OCH_2- and -CH_2Br), 6.31-8.12 (m, 19H, ArH).

CZ-G2-OH (5) It was prepared from (4) (2.20 equiv.), 3,5-dihydroxybenzyl alcohol (1.00 equiv.), potassium carbonate (2.20 equiv.) and 18-crown-6 (0.2 equiv.) in refluxing acetone under nitrogen with vigorous stirring for 48 h or until the reaction was complete. The product was purified by column chromatography on silica gel (dichloromethane/ethyl ether 40/1 as eluent) to give (5) as a white solid: yield 88%; IR υ 3350, 3056, 2932, 2900, 2868, 2199, 1623, 1375, 1289, 1122, 1059, 1021, 997, 933, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.28-2.32 (m, 8H, -CH_2-), 3.85-3.89 (m, 8H, -NCH2-), 4.50-4.54 (m, 8H, -OCH_2), 4.63 (m, 2H, –CH_2OH), 4.94 (s, 4H, -OCH_2Ar), 6.32-8.10 (m, 41H, ArH); MS (MALDI-TOF): m/z 1236.1 (M + Na^+), 1252.0 (M + K^+), calcd. m/z 1213.46; Anal. calcd. for $C_{81}H_{72}N_4O_7$ C, 80.16; H 5.99; N 4.62; Found: C, 80.28; H 6.02; N 4.58.

CZ-G2-Br (6) It was prepared from (5) (1.00 equiv.), requiring 4 × 1.25 equiv. of carbon tetrabromide (CBr_4) and triphenylphosphine (PPh_3), respectively, the product was purified by column chromatography eluting with petroleum ether/dichloromethane (2/3) to give (5) as a white solid: yield 89%; ^{1}H NMR ($CDCl_3$) δ 2.29-2.32 (m, 8H, -CH_2-), 3.85-3.89 (m, 8H, -NCH_2-), 4.42-4.54 (m, 10H, -OCH_2- and -CH_2Br), 4.93 (s, 4H, -OCH_2Ar), 6.32-8.10 (m, 41H, ArH).

CZ-G3-OH (7) It was prepared from (6) (2.20 equiv.), 3,5-dihydroxybenzyl alcohol (1.00 equiv.), potassium carbonate (2.20 equiv.) and 18-crown-6 (0.2 equiv.) in refluxing acetone under nitrogen with vigorous stirring for 48 h or until the reaction was complete. The product was purified by column chromatography on silica gel (dichloromethane/ethyl ether 80/1 as eluent) to give (7) as a white solid: yield 74%; IR υ 3350, 3056, 2932, 2900, 2868, 2199, 1594, 1483, 1347, 1260, 1191, 1059, 997, 933, 799 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.23-2.27 (m, 16H, -CH_2-), 3.80-3.83 (m, 16H, -NCH_2-), 4.44-4.48 (m, 16H, -OCH_2), 4.54 (d, 2H, –CH_2OH), 4.90-4.95 (m, 12H, -OCH_2-), 6.28-8.06 (m, 85H, ArH); MS (MALDI-TOF): m/z 2551.7 (M + Na^+), 2567.8 (M + K^+), calcd. m/z 2531.03; Anal. calcd. for $C_{169}H_{148}N_8O_{15}$ C, 80.18; H 5.90; N 4.43; Found: C, 80.21; H 5.86; N 4.36.

Scheme 2



General Procedure for the Synthesis of CZ-G*n*-NBD system. The reactions were carried out on scales of about 400 mg. A mixture of the appropriate dendritic benzyl alcohol, CZ-G*n*-OH (1.00 equiv.), 2-(methoxycarbonyl)bicycle[2.2.1]hepta-2,5-diene-3-carboxylicacid (MNBD-COOH) (11) (3.00 equiv.),

DCC(3.00 equiv.) and 4-dimethylaminopyridine (0.1 equiv.) in dry CH_2Cl_2 was stirred under nitrogen and in dark for 24 hrs. The reaction mixture was diluted by CH_2Cl_2 and partitioned between water and CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2 three times. The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

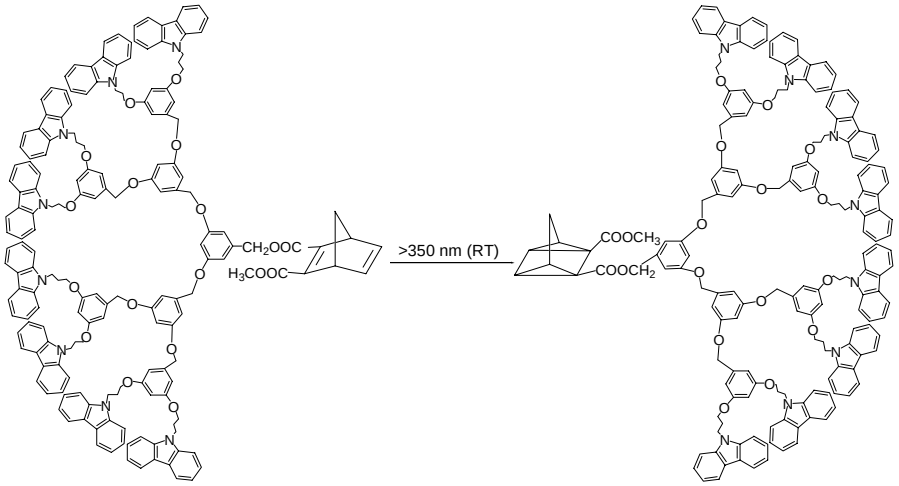
CZ-G1-NBD (8) It was prepared from (3) and (11), and purified by column chromatography on silica gel (dichloromethane/petroleum ether 8/1 as eluent) to give (8) as a white amorphous powder: yield 76%; IR υ 3056, 2932, 2900, 2868, 2199, 1707, 1623, 1375, 1289, 1122, 1059, 1021, 997, 933, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09-2.21 (m, 2H, NBD bridge H), 2.27-2.36 (m, 4H, -CH_2-), 3.55 (s, 3H, -OCH_3), 3.88-3.96 (m, 6H, NBD bridgehead H and –NCH_2-), 4.53-4.57 (m, 4H, -OCH_2-), 5.11 (s, 2H, -$COOCH_2Ar$), 6.34-6.52 (m, 3H, ArH), 6.90-6.91 (s, 2H, NBD olefinic H), 7.18-8.11 (m, 16H, CZ ArH); MS: m/z 730 (M^+), calcd. m/z 730.85; Anal. calcd. for $C_{47}H_{42}N_2O_6$ C, 77.22; H 5.80; N 3.83; Found: C, 77.20; H 5.93; N 3.85.

CZ-G2-NBD (9) It was prepared from (5) and (11), and purified by column chromatography eluting with 8/2 dichloromethane/petroleum ether (gradually increasing to 8/1) to give (9) as a white glassy solid: yield 73%; IR υ 3429, 3055, 2934, 2871, 2200, 1707, 1591, 1486, 1449, 1323, 1154, 1059, 749 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.08-2.10 (d, 2H, NBD bridge H), 2.27-2.33 (m, 8H, -CH_2-), 3.63 (s, 3H, -OCH_3), 3.86-3.92 (m, 10H, NBD bridgehead H and –NCH_2-), 4.50-4.55 (m, 8H, -OCH_2-), 4.95 (s, 4H, -OCH_2Ar), 5.16 (s, 2H, -$COOCH_2Ar$), 6.32-6.63 (m, 9H, ArH), 6.91 (s, 2H, NBD olefinic H), 7.18-8.10 (m, 32H, CZ ArH); MS (MALDI-TOF): m/z 1411.7 ($M + Na^+$), 1427.7 ($M + K^+$), calcd. m/z 1389.63; Anal. calcd. for $C_{91}H_{80}N_4O_{10}$ C, 78.64; H 5.81; N 4.03; Found: C, 78.07; H 5.96; N 4.03.

CZ-G3-NBD (10) It was prepared from (7) and (11), and purified by column chromatography eluting with 8/5 tetrahydrofuran/petroleum ether (gradually increasing to 8/1) to give (10) as a white glassy solid: yield 71%; IR υ 3429, 3055, 2932, 2900, 2868, 2199, 1707, 1594, 1483, 1347, 1153, 1059, 933, 799 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.05 (d, 2H, NBD bridge H), 2.24-2.27 (m, 16H, -CH_2-), 3.61 (s, 5H, -OCH_3 and NBD bridgehead H), 3.81-3.84 (m, 16H, –NCH_2-), 4.45-4.49 (m, 16H, -OCH_2-), 4.91-4.96

(m, 10H, -OCH_2Ar), 5.19 (s, 2H, -$COOCH_2Ar$), 6.29-6.91 (m, 27H, NBD olefinic H, ArH and-OCH_2Ar), 7.16-8.07 (m, 64H, CZ ArH) ; MS (MALDI-TOF): m/z 2728.3 ($M + Na^+$), 2744.2 ($M + K^+$), calcd. m/z 2707.20; Anal. calcd. for $C_{179}H_{156}N_8O_{18}$ C, 79.40; H 5.81; N 4.14; Found: C, 77.36; H 6.01; N 3.88.

Scheme 3



General Procedure for the isomerization of NBD to QC in CZ-G*n*-NBD. *CZ-Gn-QC* was prepared from CZ-G*n*-NBD and these reactions were performed on scales of about 150mg. Photoirradiation was performed in a Pyrex reactor, and the samples were purged with argon. A 500-W middle-high-pressure mercury lamp was used as the excitation source. A WB-350 glass filter was used to cut off the light with wavelength less than 350 nm. The process of the reaction was monitoring by TLC. After irradiation, the solvent was evaporated from the samples under reduced pressure. The product was purified by preparative thin-layer chromatography, and characterized by IR, ^1H NMR and mass spectroscopies.

CZ-G1-QC (12) It was prepared from CZ-G1-NBD (8) and purified by column chromatography eluting with 40/1 dichloromethane/ethyl ether to give (12) as a white amorphous powder: yield 98%; IR υ 3429, 3055, 2934, 2871, 2200, 1707, 1591, 1486, 1449, 1323, 1154, 1059, 749, 717 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12-2.50 (m, 10H, QC H and –CH_2-), 3.54 (s, 3H, -OCH_3), 3.89-3.92 (m, 4H, -NCH_2-), 4.53-4.57 (m, 4H, -OCH_2), 5.03-5.05 (m, 2H, -$COOCH_2Ar$), 6.33-8.11 (m, 19H, ArH); MS: m/z 730 (M^+), calcd. m/z 730.85.

CZ-G2-QC (13) It was prepared from CZ-G2-NBD (9) and purified by column chromatography eluting with 40/1 dichloromethane/ethyl ether to give (13) as a white amorphous powder: yield 96%; IR υ 3429, 3055, 2934, 2871, 2200, 1707, 1591, 1486, 1449, 1323, 1154, 1059, 749, 717 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.08-2.47 (m, 14H, QC H and $–CH_2$-), 3.59 (s, 3H, -OCH_3), 3.85-3.89 (m, 8H, -NCH_2-), 4.50-4.54 (m, 8H, -OCH_2-), 4.94 (s, 4H, $ArOCH_2Ar$), 5.01-5.02 (m, 2H, -$COOCH_2Ar$), 6.36-8.11 (m, 41H, ArH); MS (MALDI-TOF): m/z 1411.4 ($M + Na^+$), 1427.3 ($M + K^+$), calcd. m/z 1389.63.

CZ-G3-QC (14) It was prepared from CZ-G3-NBD (10) and purified by column chromatography eluting with 60/1 dichloromethane/ethyl ether to give (14) as a white amorphous powder: yield 86%; IR υ 3429, 3055, 2934, 2871, 2200, 1707, 1591, 1486, 1449, 1323, 1154, 1122, 1059, 799, 746 cm^{-1}; ^1H NMR ($CDCl_3$) δ2.06-2.44 (m, 22H, QC H and $–CH_2$-), 3.58 (s, 3H, -OCH_3), 3.81-3.85 (m, 16H, -NCH_2-), 4.46-4.50 (m, 16H, -OCH_2-), 4.91-4.97 (m, 12H, $ArOCH_2Ar$), 4.99-5.00 (m, 2H, -$COOCH_2Ar$), 6.30-8.07 (m, 85H, ArH); MS (MALDI-TOF): m/z 2727.8 ($M + Na^+$), calcd. m/z 2707.20.

References

(1) (a) Wooley, K. L.; Hawker, C. J. Fréchet, J. M. J. *J. Am. Chem. Soc.* **1993**, *115*, 11496. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010. (c) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.

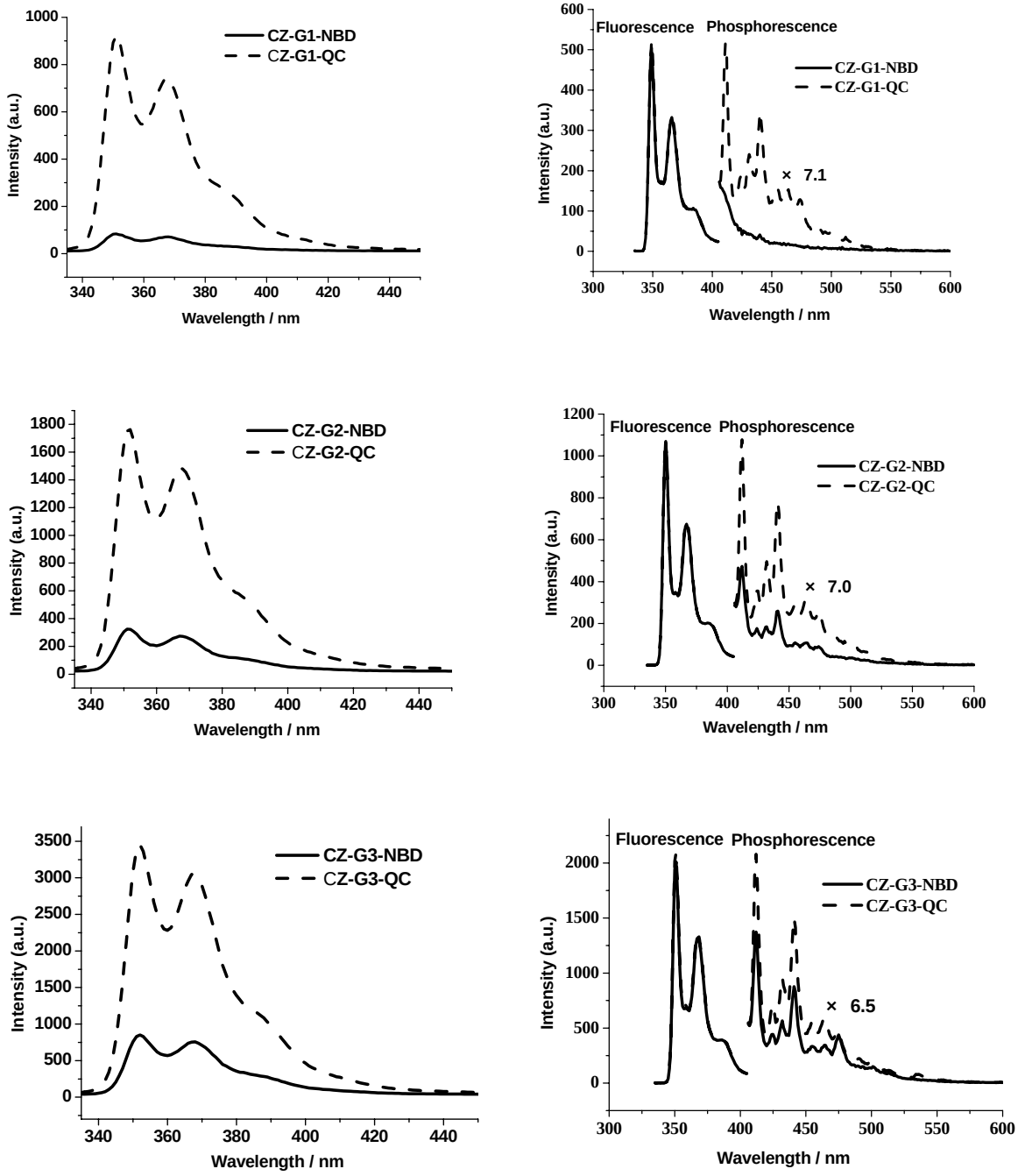


Figure 1. Emission spectra of CZ-G*n*-NBD and CZ-G*n*-QC in CH_2Cl_2 at RT (left) and in MTHF at 77K (right), respectively, λ_{ex} = 330 nm, [CZ-G*n*-NBD] = [CZ-G*n*-QC] = 1.0×10^{-5} M.

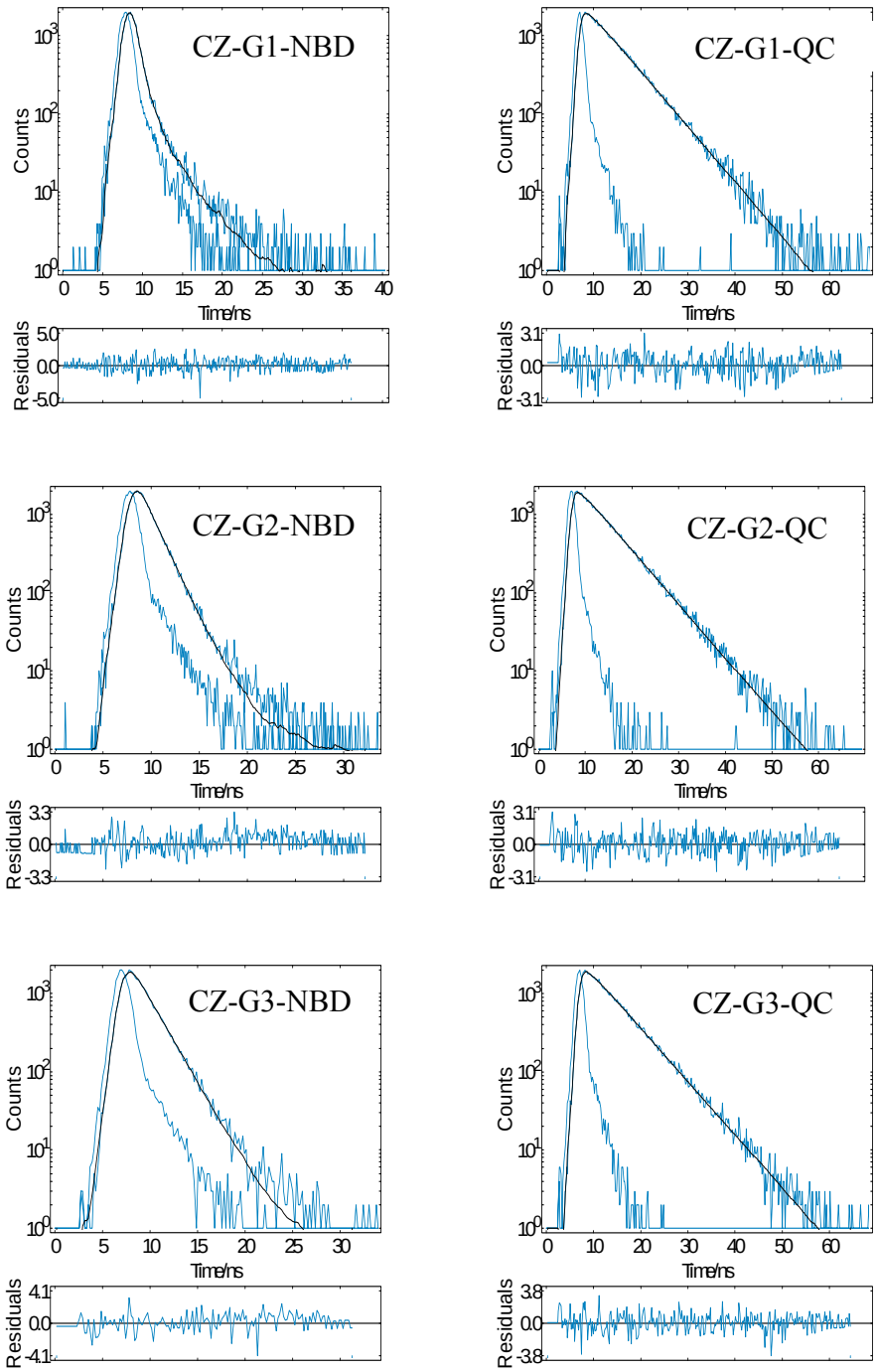


Figure 2. Fluorescence decay traces of CZ-G*n*-NBD and CZ-G*n*-QC in CH_2Cl_2 at ambient with excitation λ_{ex} = 330 nm and the detection λ = 352 nm. [CZ-G*n*-NBD] = [CZ-G*n*-QC] = 1.0×10^{-5} M. The sharp decay curve is the lamp profile, and the black solid line is the fitted curve. The bottom trace shows the residuals distribution for the monoexponential fit.

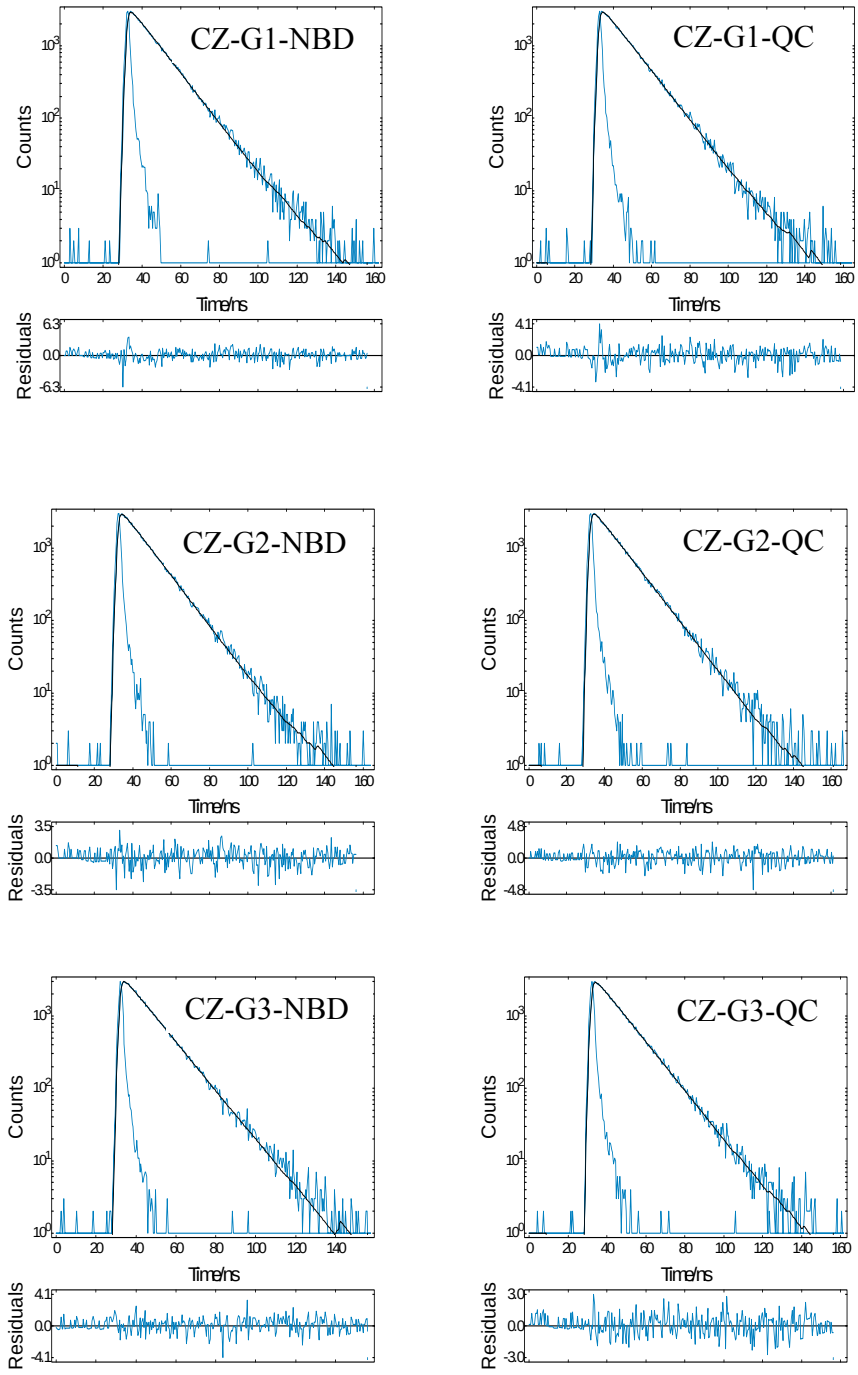


Figure 3. Fluorescence decay traces of CZ-G*n*-NBD and CZ-G*n*-QC in MTHF at 77K with excitation λ_{ex} = 330 nm and the detection λ = 441 nm. [CZ-G*n*-NBD] = [CZ-G*n*-QC] = 1.0×10^{-5} M. The sharp decay curve is the lamp profile, and the black solid line is the fitted curve. The bottom trace shows the residuals distribution for the monoexponential fit.