Dendritic incorporation of quinacridone: solubility, aggregation, electrochemistry, and solid state luminescence

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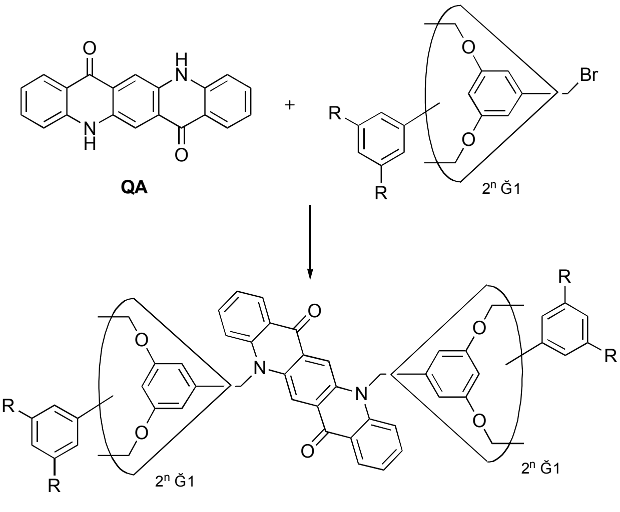
The first incorporation of quinacridone, a technologically important organic emitter, into dendrimers increases solubility, decreases self-association, retards heterogeneous electron transfer, and enhances solid state luminescence.

Experimental procedures and characterization data for quinacridone dendrimers: **Method A:** To a rapidly stirred solution of quinacridone (1 equiv.) in dry DMF was slowly added NaH (5.5 equiv.). [G-*n*]-Br (2.7 equiv.) was then added to the reaction mixture which was then maintained at reflux (80 °C) for 26 h. The mixture was poured onto ice, the majority of solvent was evaporated and the crude product was isolated by filtration and extraction of the filtrate (CH_2Cl_2). Purification by flash chromatography (SiO_2, CH_2Cl_2) followed by precipitatation into methanol from CH_2Cl_2 gave an orange solid. **Method B:** To a stirred mixture of quinacridone (1 equiv.), TBAI (4 equiv.) in 100:1 v/v toluene-50% aqueous NaOH was added [G-*n*]-Br (2.3 equiv.) and the reaction mixture was maintained at reflux (80°C) for 32 h. Isolation and purification followed Method A.

*[G-1]$_2$-QA (***1***)*: To a rapidly stirred solution of quinacridone (156 mg, 0.488 mmol) in dry DMF (25 mL) was slowly added NaH (80 mg, 2.7 mmol). [G-1]-Br (0.507 g, 1.30 mmol) was then added to the reaction mixture which was then maintained 80 °C for 26 h. The reaction was quenched by pouring onto ice (ca. 100 g). The majority of DMF was evaporated in vacuo and the resulting slurry was filtered to yield an orange solid. The orange solid was dissolved in CH_2Cl_2 (ca 100 mL). The aqueous filtrate was washed with CH_2Cl_2 (3 x 50 mL) the organic layer was separated, and all organic layers were combined. This solution was dried ($MgSO_4$), filtered, and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) followed by precipitatation into methanol from CH_2Cl_2 to yield **1** as an orange solid (180 mg, 41 %); IR (KBr) 1627, 1604, 1494, 1452 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.46 (s, 2H), 8.32 (d, J = 7.6 Hz, 2H), 7.75 (t, J = 7.32 Hz, 2H), 7.55 (d, J = 8.79 Hz, 2H), 7.25 (m, 12H), 6.62 (s, 2H), 6.48 (s, 2H), 5.77 (s, 4H), 4.98 (s, 8H); MS (MALDI) m/z 917.32 (M+H$^+$, $C_{62}H_{49}N_2O_6$ requires 917.36).

*[G-2]$_2$-QA (***2***)*: To a stirred mixture of quinacridone (110 mg, 0.336 mmol), tetrabutylammonium iodide (0.257 g, 0.697 mmol), and freshly distilled toluene (10 mL) was added 50% aqueous NaOH (0.4 mL). After slow addition of [G-2]-Br (0.71 g, 0.88 mmol) the reaction mixture was maintained at 80 °C for 32 h. The reaction was quenched with H_2O (20 mL) and filtered to give an orange solid that was washed with H_2O (20 mL) and methanol (20 mL). The filtrate was extracted with CH_2Cl_2 and the organic layer was dried ($MgSO_4$), filtered, and concentrated. The residue was combined with the previously isolated orange solid and the combined sample was purified by flash chromatography (SiO_2, CH_2Cl_2) followed by precipitation into methanol from CH_2Cl_2. The precipitate was filtered to yield **2** as an orange solid (0.40 g, 69 %); IR (KBr) 1629, 1599, 1495, 1454 cm^{-1}; δ_H (300 MHz, DMSO-d_6): 8.41 (s, 2H), 8.26 (d, J = 8.1 Hz, 2H), 7.68 (t, J = 7.6 Hz, 2H), 7.49 (d, J = 9.03 Hz, 2H), 7.27 (m, 40H), 6.59 (s, 2H), 6.54 (s, 4H), 6.482 (s, 2H), 6.41 (s, 2H), 5.67 (s, 2H), 4.93 (s, 8H), 4.88 (s, 4H); MS (MALDI) m/z 1766.68 (M+H$^+$, $C_{118}H_{97}N_2O_{14}$ requires 1766.70).

*[G-3]$_2$-QA (***3***)*: Following the procedure described for the preparation of **2**, quinacridone (0.40 g, 1.26 mmol), [G-3]-Br (4.40 g, 2.65 mmol), tetrabutylammonium iodide (1.86 g, 5.04 mmol), 50% aqueous NaOH (0.5 mL), and toluene (40 mL) yielded, after purification by flash chromatography (SiO_2, CH_2Cl_2) and precipitation from hot 4:1 hexanes-CH_2Cl_2, **3** as an orange solid (2.63 g, 60%); IR (KBr) 1629, 1605, 1497, 1454 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.49 (s, 2H), 8.45 (d, J = 8.1 Hz, 2H) 7.53 (t, J = 8.4 Hz, 2H) 7.30 (m, 80H), 7.116 (t, 7.5 Hz, 2H), 6.63 (d, J = 1.8 Hz, 16H), 6.53 (t, J = 2.1 Hz, 8H) 6.48 (d, J = 1.8 Hz, 8H) 6.36 (t, J = 1.8 Hz, 4H) 5.46 (s, 4H) 4.97 (s, 32H) 4.79 (s, 24H); MS (MALDI) m/z 3464.37 (M+H$^+$, $C_{230}H_{193}N_2O_{30}$ requires 3464.37).



R = H	R = t-Bu
1: (n = 1)	**4**: (n = 0)
2: (n = 2)	**5**: (n = 1)
3: (n = 3)	**6**: (n = 2)
	7: (n = 3)

Scheme 1 Synthesis of dendritic quinacridones.

*t-Bu[G-0]$_2$-QA (***4***)*: Following the procedure described for the preparation of **2**, quinacridone (1.45 g, 4.7 mmol), 3,5-di-*tert*-butylbenzyl bromide (3.07 g, 10.8 mmol), tetrabutylammonium iodide (6.94 g, 18.8 mmol), 50% aqueous NaOH (1.5 mL), and toluene (70 mL) yielded **4** as an orange solid (2.64 g, 76%) after purification by flash chromatography (Si_2O, CH_2Cl_2); IR (KBr) 1630, 1605, 1494, 1454 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.75 (s, 2H), 8.55 (d, J = 1.2 Hz, 1H), 8.52 (d, J = 1.5 Hz, 1H), 7.65 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 7.33 (s, 2H), 7.25 (t, J = 7.7 Hz, 2H), 7.06 (s, 4H), 5.77 (s, 4H), 1.22 (s, 36H); MS (MALDI) m/z 716.26 (M$^+$, $C_{50}H_{56}N_2O_2$ requires 716.43).

*t-Bu[G-1]$_2$-QA (***5***)*: Following the procedure described for the preparation of **2**, quinacridone (1.48 g, 4.75 mmol), (3,5-*t*Bu)$_4$[G-1]-Br (6.68 g, 10.9 mmol), tetrabutylammonium iodide (7.02 g, 19.0 mmol), 50% aqueous NaOH (1.0 mL), and toluene (200 mL) yielded **5** as an orange solid (4.94 g, 76%) after purification by flash chromatography (SiO_2, CH_2Cl_2); IR (KBr) 1634, 1604, 1495, 1454 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.72 (s, 2H), 8.55 (d, J = 1.5 Hz, 1H), 8.52 (d, J = 1.5 Hz, 1H), 7.66 (t, J = 7.8 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.37 (t, J = 1.8 Hz, 2H), 7.28 (t, 7.5 Hz, 2H), 7.22 (d, J = 2.1 Hz, 4H), 6.62 (t, 2H), 6.54 (d, J = 1.8 Hz), 5.71 (s, 4H), 4.92 (s, 8H), 1.29 (s, 72H); MS (MALDI) m/z 1365.81 (M+H$^+$, $C_{94}H_{113}N_2O_6$ requires 1365.86).

*t-Bu[G-2]$_2$-QA (***6***)*: Following the procedure described for the preparation of **2**, quinacridone (0.58 g, 1.85 mmol), (3,5-*t*Bu)$_8$[G-2]-Br (5.40 g, 4.27 mmol), tetrabutylammonium iodide (2.73 g, 7.4 mmol), 50% aqueous NaOH (0.7 mL), and toluene (125 mL) yielded **6** (3.38 g, 69%) after purification by flash chromatography (SiO_2, CH_2Cl_2) and precipitation into methanol from CH_2Cl_2; IR (KBr) 1633, 1606, 1495, 1455 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.65 (s, 2H), 8.52 (d, J = 1.5 Hz, 1H), 8.50 (d, J = 1.8 Hz), 7.61 (t, J = 7.8 Hz, 2H), 7.39 (t, J = 1.8 Hz, 6H), 7.34 (d, J = 9.0 Hz, H), 7.26 (d, J = 2.1 Hz, 12H), 7.20 (t, J = 7.8 Hz 2H), 5.62 (s, 4H), 4.95 (s, 16H), 4.91 (s, 8H), 1.29 (s, 144H); MS (MALDI) m/z 2662.38 (M$^+$, $C_{182}H_{224}N_2O_{14}$ requires 2662.69).

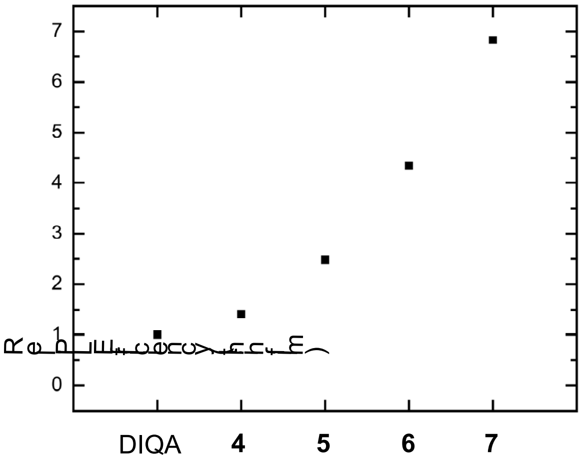


Fig. S1 PL efficiency of neat thin films of dendrimers **4–7** relative to DIQA. The relative PL efficiency was measured by integrating the corrected PL spectrum (λ_{ex} = 470 nm) and dividing by the absorbance at 470 nm. This value was then divided by the analogous value for a DIQA film.

t-Bu[G-3]$_2$-QA (7): Following the procedure described for the preparation of **2**, quinacridone (0.24g, 0.778 mmol), (3,5-*t*Bu)$_{16}$[G-3]-Br (4.3 g, 1.634 mmol), tetrabutylammonium iodide (1.15 g, 3.11 mmol), 50% aqueous NaOH (0.8 mL), and toluene (50 mL) yielded **7** (1.30g, 30%), after purification via flash chromatography (SiO_2, 1:9 THF:Hexanes followed by 2:1 CH_2Cl_2:Hexanes) followed by precipitation from CH_2Cl_2 into a mixture of DMF/H_2O (1:2); IR (KBr) 1632, 1597, 1496, 1454 cm^{-1}; δ_H (300 MHz, $CDCl_3$): 8.62 (s, 1H), 8.48 (d , 8.1 Hz , 2H), 7.56 (t , 7.2 Hz , 2H), 7.38 (t , 1.5 Hz , 16H), 7.25 (d , 1.5 Hz , 32H), 7.32 (d , 9.3 Hz , 2H) 7.15 (t , 7.2 Hz , 2H), 6.71 (d , 1.8 Hz , 16H), 6.63 (t , 2.1 Hz , 8H), 6.61 (d , 1.8 Hz , 8H), 6.57 (t , 2.1 Hz , 2H), 6.51 (t , 1.8 Hz , 4H), 6.54 (d , 1.8 Hz , 4H), 5.62 (s, 4H), 4.98 (s, 32H), 4.91 (s, 16H), 4.88 (s, 8H), 1.31 (s, 288H), MS (MALDI), m/z (M^+, $C_{358}H_{448}N_2O_{30}$ requires 5258.37)

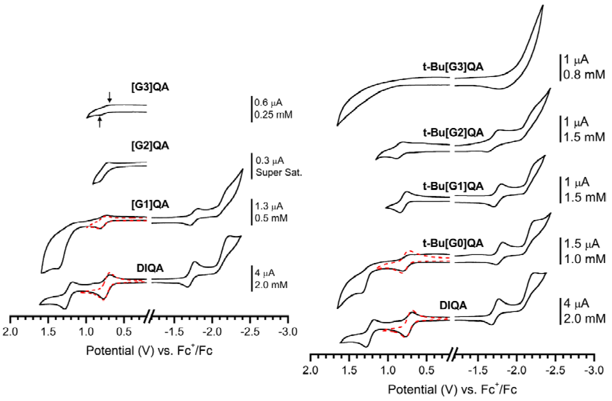


Fig. S2 (l.) Cyclic voltammograms of **4–7** at a 0.5 mm diameter Pt disc electrode in N_2-degassed CH_2Cl_2 with 0.1 M TBAHFP supporting electrolyte. Potential scan rate 100 mV sec^{-1}, Fc/Fc$^+$ reference. Dashed lines represent CVs for the first oxidation process only. (r.) Cyclic voltammograms of **1–3** under the same conditions.