

Supporting Information

A Stable Aggregate System of Silyl Ether Substituted Quinacridone and Its Aggregation-state Changes Induced by Fluoride-ion: Inspiration for A Dual Guaranteed Strategy for Probe Design

Peng Chen,^{a,b} Guo-Jie Liu,^a Yuyang Wang^a and Sean Xiao-An Zhang*^a

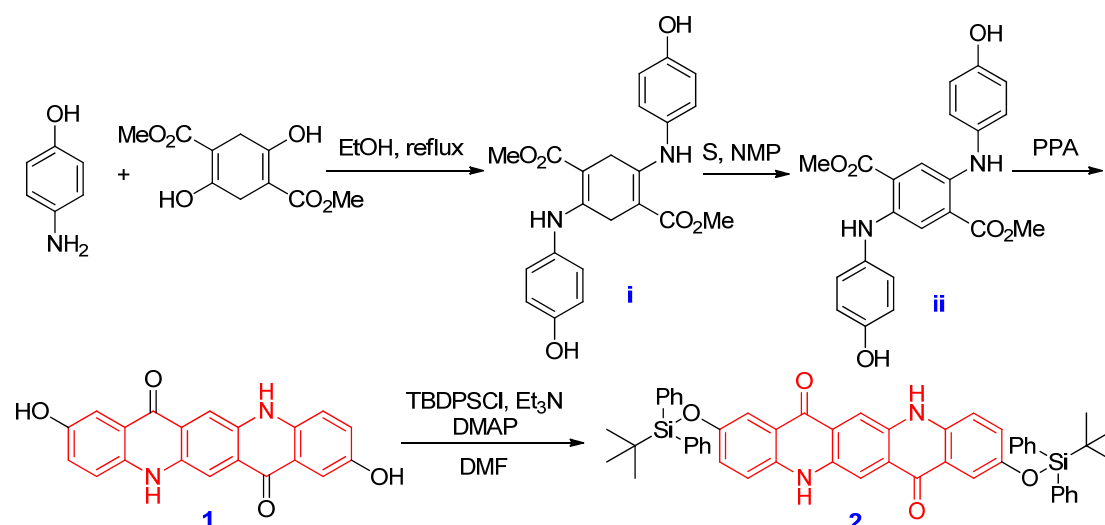
[a] State Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China. Tel: +86-431-85153812; E-mail: seanzhang@jlu.edu.cn.

[b] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China.

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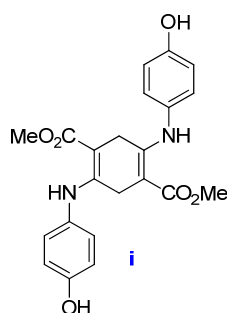
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1. Synthesis of 2,9-di(*tert*-butyldiphenylsilyloxy) quinacridone (2)



NMP = N-Methyl pyrrolidone, PPA = polyphosphoric acid, TBDPSCI = *tert*-butylchlorodiphenylsilane, DMAP = 4-dimethylaminopyridine.

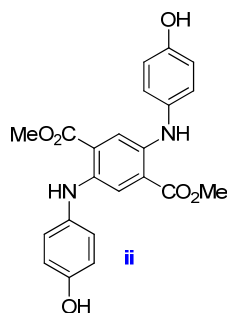
Dimethyl 2,5-bis(p-hydroxyanilino)-3,6-dihydro terephthalate (i)



Dimethyl succinylsuccinate (5.0 g, 21.9 mmol) and *p*-aminophenol (7.12 g, 65.2 mmol, 3.0 equiv) were suspended in ethanol (150 mL). The resulting reaction mixture was then refluxed and stirred under argon until dimethyl succinylsuccinate disappeared (about 12 h). After cooling to room temperature, the mixture was concentrated under reduced pressure. The resulting residue was filtered, washed with water and cold ethanol, dried in vacuum, affording the expected compound **i** (7.58 g, 84 % yield). The NMR spectrum is in good correspondence with literature data¹.

¹H NMR (300 MHz, DMSO-*d*₆): δ = 10.28 (s, 2H), 9.51 (s, 2H), 6.99 (d, J = 8.7 Hz, 4H), 6.77 (d, J = 8.7 Hz, 4H), 3.54 (s, 6H), 3.17 (s, 4H) ppm.

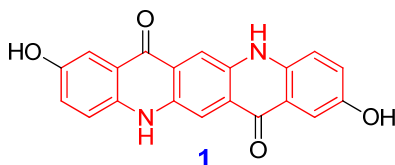
Dimethyl 2,5-bis(p-hydroxyanilino)-terephthalate (ii)



To a solution of **i** (5.0 g, 12.2 mmol) in N-Methyl pyrrolidone (30 mL) was added sulfur (0.78 g, 24.33 mmol, 2.0 equiv). The resultant reaction mixture was then heated to 115 °C and stirred under argon for 3 h. After cooling to room temperature, the mixture was poured into 250 mL of water under vigorous stirring. The resulting precipitate was washed with water and dried in vacuum, giving compound **ii** (4.0 g, 80% yield). The NMR spectrum is in good correspondence with literature data¹.

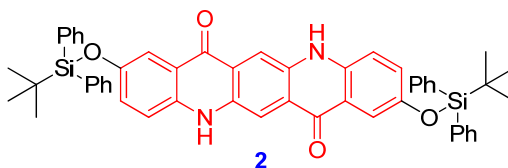
¹H NMR (300 MHz, DMSO-*d*₆): δ = 9.26 (s, 2H), 8.25 (s, 2H), 7.50 (s, 2H), 6.99 (d, J = 8.7 Hz, 4H), 6.76 (d, J = 8.7 Hz, 4H), 3.77 (s, 6H) ppm.

2,9-Dihydroxy quinacridone (1)¹



20 mL of polyphosphoric acid (PPA) in round-bottom flask was heated to 80 °C. Then to the above system was added **ii** (1.0 g, 2.45 mmol) under argon. After removing air thoroughly by repeated evacuation/argon-flushing cycles, the reaction mixture was heated to 135 °C and stirred for 4 h. Then the mixture was cooled to 80 °C and poured into 100 mL of hot water. The resulting suspension was cooled to room temperature. Then the precipitate was filtered, washed with water and dried in vacuum, affording the crude compound **1** (759 mg, 90 % yield). The crude compound **1** was directly used for next step without further purification.

2,9-di(*tert*-butyldiphenylsilyloxy) quinacridone (**2**)



The crude compound **1** (1.0 g, 2.99 mmol), *tert*-butylchlorodiphenylsilane (3.30g, 11.96 mmol, 4.0 equiv), triethylamine (2.5mL, 17.94 mmol, 6.0 equiv) and 4-dimethylaminopyridine (0.73 g, 5.98 mmol, 2.0eq) was added into DMF (50 mL) under argon, and the resulting reaction mixture was stirred at room temperature overnight. After removing DMF under high vacuum while stirring, to the resulting residue was added CH₂Cl₂ (20 mL) and water (20 mL). Then, the precipitate was filtered, washed with CH₂Cl₂, water and Et₂O, dried in vacuum, affording the compound **2** (1.91g, 80% yield).

¹H NMR (300 MHz, CD₃OD): δ = 8.34 (s, 2H), 8.10 (d, J = 2.6 Hz, 2H), 7.85–7.80 (m, 8H), 7.42 (dd, J = 9.0, 2.6 Hz, 2H), 7.34–7.27 (m, 12H), 7.19 (d, J = 9.0 Hz, 2H), 1.11 (s, 18H) ppm; ¹H NMR (300 MHz, DMSO-*d*₆, 1.42M): δ = 11.66 (s, 2H), 8.42 (s, 2H), 8.05 (d, J = 2.5 Hz, 2H), 7.82–7.79 (m, 8H), 7.62 (dd, J = 9.0, 2.5 Hz, 2H), 7.39–7.27 (m, 14H), 0.96 (s, 18H) ppm; ¹³C NMR (125 MHz, DMSO-*d*₆): δ = 176.5, 147.7, 137.5, 135.0, 134.7, 134.5, 129.3, 127.5, 127.3, 123.7, 119.0, 117.4, 115.0, 113.0, 26.5, 19.2 ppm; IR: ν = broad band 3680–3110 peaking at 3380, 3075, 3050, 2960, 2930, 2890, 2860, 1615–1550, 1475, 1210, 1090, 880, 700 cm⁻¹; MS (ESI): m/z calcd for C₅₄H₅₂N₃O₄Si₂ [$M+H+CH_3CN$]⁺: 862.3; found: 862.2 [$M+H+CH_3CN$]⁺.

2. References

1. P. H. Liu, T. He and C. P. Chang, *J. Photochem. Photobiol. A Chem.*, 2000, **137**, 99-104.

3. Copies of NMR Spectra

