Research Article

Photooxygenations and Self-Sensitizations of Naphthylamines: Efficient Access to Iminoquinones

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A series of spiro [fluorene-9,7'-dibenzo[c,h]acridine]-5'-one (SFDBAO) derivatives have been concisely and cleanly obtained by exposure to sunlight without external photosensitizers in the higher yields than that when using a UV lamp. An interesting autocatalyst and self-sensitive procedure have been proposed to explain the effective photooxygenation. SFDBAO derivatives exhibit the continuous π -stacks in single-crystal and electron-withdraw properties with red light-emitting and photovoltaic properties.

1. Introduction

Iminoquinones constitute the core structures of many naturally occurring compounds and display important antineoplastic, antifungal, and antibacterial activities (Figure 1) [1–4]. Commonly used approaches for the construction of iminoquinones include (i) metal catalysis [5–7], (ii) photosynthesis by UV lamps and photosensitizers [7], (iii) 2-iodoxybenzoic acid [IBX, 1-hydroxy-1,2-benziodoxol-3(1H)-one 1-oxide] oxidation [8, 9], and (iv) Dess–Martin periodinane [DMP, 1,1,1-triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1H)-one]-mediated oxidative reaction [10]. Although the aforementioned elegant methods appear to be general and efficient, further development of the low-cost and eco-friendly methods that allow the facile assembly of highly functionalized iminoquinone from readily available and simple starting materials is still required, because they have wide range of applications in medicine and biology.

Herein, we report a photochemical strategy for generating excited state species from naphthylamines, which does not rely upon any metal- or organic-based photoredox catalysts (Scheme 1). The reaction, which occurs at ambient

temperature and requires irradiation by sunlight in order to proceed, is sufficient for achieving iminoquinones with synthetically useful results. In general, most photooxygenations require the effective photocatalysis or photosensitizers such as, Ir or Ru complexes [11], rose bengal [12–14], porphyrins [15], 9-mesityl-10-methylacridinium [16, 17], inorganic TiO_2 [18, 19], or organic molecule [20]. However, our visible light mediates photooxygenation of naphthylamines with the advantages of high chemoselectivity without any external photosensitizers. In this reaction, naphthylamines play a dual role of providing both photosensitizer and substrate, and O_2 functions as triplet state trapping agent and oxygen sources.

Spirofluorenes are widely used in semiconductors, including OLEDs, PLEDs, solar cells, fuel cells, memories, and so on [21]. Common electron-rich spirofluorenes include spirobifluorenes, spirofluoreneacridines, spirobisindane, spirofluorenexanthenes, spiropyran, and so on. Till now, electron-deficient spirofluorenes have not been synthesized and reported because of the lack of convenient and efficient synthetic route. Therefore, we describe a novel strategy for the one-pot synthesis of electron-deficient

FIGURE 1: Bioactive molecules containing iminoquinone constitute the core structures.

SCHEME 1: Photooxygenations and self-sensitizations of naphthylamine strategies. (a) Previous work [4]. (b) Our work.

5*H*-spiro[dibenzo[*c,h*]acridine-7,9'-fluorene]-5-one (SFDBAO) through a photooxygenation-initiated cascade process.

2. Experimental

2.1. Reagents and Instruments. All the reagents used were of analytical pure. The UV lamp irradiation is carried out indoors by a household 23 W compact fluorescent light (CFL) bulb. ^1H and ^{13}C NMR spectra were performed on a Bruker 400 MHz spectrometer in CDCl_3 or $\text{DMSO}-d_6$ with tetramethylsilane (TMS) as the interval standard. Mass spectra were recorded on a Shimadzu GCMS-QP2010 plus equipped with DB-5 ms column or a Shimadzu AXIMA-CFR plus spectrometer. For the MALDI-TOF MS spectra, the spectra were recorded in reflective mode, and substrates were used. Molecular weights of the samples were measured by gel permeation chromatography (GPC) on a Shimadzu LC-20A HPLC system equipped with 7911GP-502 and GPNXC columns. Elemental analyses were carried out in an Elementar Analysensysteme GmbH-vario EL III element analyzer. Absorption spectra were measured with a Shimadzu UV-3600 spectrometer at 25°C , and emission spectra were recorded on a Shimadzu RF-5301(PC)S luminescence spectrometer. Cyclic voltammetric (CV) studies were conducted using a CHI660C electrochemical workstation in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. X-ray crystallographic data were collected at 293 K on a P4 Bruker diffractometer equipped with a fine-focus sealed tube and a rotating anode utilizing graphite-monochromated $\text{Mo } K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing was carried out using the program SAINT, while the program SADABS was utilized for the scaling of diffraction data, the application of a decay correction, and an empirical absorption correction based on redundant reflections. The structures were solved by direct methods and refined against F^2 with the full-matrix, least-squares methods using SHELXS-97 and SHELXL-97, respectively. Column chromatography purification was carried out using the silica gel (200–300 mesh).

2.2. Syntheses of the Intermediates and the Target Compounds

2.2.1. General Procedure for Preparation of 2 and 3. In a round bottom flask, compound **1** (2 mmol) was dissolved in MeCN (400 mL) and the mixture was stirred in the sunlight irradiation under air atmosphere for 6 hours to produce compound **2**. The crude product was purified by flash column chromatography (silica gel, CH_2Cl_2 /petroleum ether, 1: 3) to give purified products.

(1) *Spiro[fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one* (SFDBAO, **2a**). This compound was prepared following the general procedures by applying **1a** (0.862 g, 2 mmol) to give **2a** (0.69 g, 1.56 mmol) as a red solid with the yield of 78%. GC-MS (EI- m/z) calcd for $\text{C}_{33}\text{H}_{19}\text{NO}^+ [\text{M}]^+$ 445.15, found 445.00. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.28–9.26 (*d*, $J = 8.4 \text{ Hz}$, 1H), 9.06–9.04 (*d*, $J = 8.8 \text{ Hz}$, 1H), 8.14–8.12 (*d*, $J = 8.8 \text{ Hz}$, 1H), 7.87–7.84 (*m*, 3H), 7.76–7.73 (*t*, $J = 9.2 \text{ Hz}$, 2H), 7.68–7.64 (*t*, $J = 8.4 \text{ Hz}$, 1H), 7.61–7.57 (*t*, $J = 7.6 \text{ Hz}$, 1H), 7.55–7.53 (*d*, $J = 8.4 \text{ Hz}$, 1H), 7.45–7.41 (*t*, $J = 7.6 \text{ Hz}$, 2H), 7.22–7.18 (*t*, $J = 7.6 \text{ Hz}$, 2H), 7.04–7.02 (*d*, $J = 7.6 \text{ Hz}$, 2H), 6.57–6.55 (*d*, $J = 8.8 \text{ Hz}$, 1H), 6.04 (*s*, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 184.5, 151.7, 150.0, 145.4, 140.8, 137.8, 135.6, 133.6, 132.7, 132.2, 131.4, 130.8, 130.3, 128.9, 128.8, 128.6, 127.7, 127.2, 126.7, 125.9, 125.3, 124.8, 124.6, 123.8, 120.7, 57.7. Anal. Calcd for $\text{C}_{33}\text{H}_{19}\text{NO}$: C, 89.04; H, 4.30; N, 3.15. Found: C, 89.07; H, 4.28; N, 3.18.

(2) *9'-Chlorospiro[fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one* (ClSFDBAO, **2b**). This compound was prepared following the general procedures by applying **1a** (0.862 g, 2 mmol) and CCl_4 (400 mL). Purified by flash column chromatography using CH_2Cl_2 :petroleum ether = 1: 3 to give **2b** (0.785 g, 1.64 mmol) as a red solid with the yield of 82%. GC-MS (EI- m/z) calcd for $\text{C}_{33}\text{H}_{18}\text{ClNO}^+ [\text{M}]^+$ 479.11, found 479.05. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.32–9.29 (*d*, $J = 7.6 \text{ Hz}$, 1H), 9.02–9.00 (*d*, $J = 8.0 \text{ Hz}$, 1H), 8.21–8.19 (*d*, $J = 8.4 \text{ Hz}$, 1H), 8.13–8.11 (*d*, $J = 7.6 \text{ Hz}$, 1H), 7.88–7.86 (*d*, $J = 7.6 \text{ Hz}$, 3H), 7.84–7.79 (*m*, 1H), 7.72–7.66 (*m*, 2H),

7.47–7.43 (*t*, *J* = 7.4 Hz, 2H), 7.24–7.20 (*t*, *J* = 7.4 Hz, 2H), 7.04–7.02 (*d*, *J* = 7.6 Hz, 2H), 6.64 (*s*, 1H), 6.02 (*s*, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): ¹³C NMR (100 MHz, CDCl₃): δ 184.4, 151.1, 150.3, 145.0, 140.7, 137.0, 135.4, 133.8, 133.2, 132.8, 131.4, 130.9, 130.9, 130.4, 129.2, 129.0, 128.9, 127.9, 127.7, 126.0, 125.3, 124.8, 124.4, 124.2, 120.9, 57.5. Anal. Calcd for C₃₃H₁₈ClNO: C, 82.73; H, 3.79; N, 2.92. Found: C, 82.76; H, 3.77; N, 2.90.

(3) 2-Bromospiro[fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one (BrSFDBAO, **2c**). This compound was prepared following the general procedures by applying **1c** (1.02 g, 2 mmol) to give **2c** (0.765 g, 1.46 mmol) as a red solid with the yield of 73%. GC-MS (EI-*m/z*) calcd for C₃₃H₁₈BrNO⁺ [*M*]⁺ 523.06, found 522.85. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.27–9.25 (*d*, *J* = 8.4 Hz, 1H), 9.05–9.03 (*d*, *J* = 7.6 Hz, 1H), 8.14–8.12 (*d*, *J* = 8.4 Hz, 1H), 7.89–7.95 (*t*, *J* = 7.6 Hz, 1H), 7.84–7.82 (*d*, *J* = 7.6 Hz, 1H), 7.80–7.75 (*m*, 2H), 7.75–7.67 (*m*, 2H), 7.62–7.54 (*m*, 3H), 7.46–7.42 (*t*, *J* = 7.6 Hz, 1H), 7.25–7.21 (*t*, *J* = 7.4 Hz, 1H), 7.14 (*s*, 1H), 7.03–7.01 (*d*, *J* = 7.6 Hz, 1H), 6.55–6.53 (*d*, *J* = 8.4 Hz, 1H), 6.02 (*s*, 1H). ¹³C NMR (101 MHz, CDCl₃): δ 184.4, 153.5, 151.5, 149.9, 144.4, 139.7, 139.7, 137.8, 135.5, 133.7, 132.9, 132.2, 131.9, 131.3, 130.9, 130.5, 130., 129.4, 128.9, 128.0, 127.8, 127.7, 127.4, 126.9, 126.0, 125.4, 124.9, 124.4, 123.8, 122.2, 122.1, 120.7, 57.5. Anal. Calcd for C₃₃H₁₈BrNO: C, 75.78; H, 3.47; N, 2.68. Found: C, 75.81; H, 3.45; N, 2.66.

(4) 2,7-Dibromospiro[fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one (DBrSFDBAO, **2d**). This compound was prepared following the general procedures by applying **1d** (1.18 g, 2 mmol) to give **2d** (0.844 g, 1.40 mmol) a red solid with the yield of 70%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.26–9.24 (*d*, *J* = 8.4 Hz, 1H), 9.05–9.03 (*d*, *J* = 7.6 Hz, 1H), 8.15–8.13 (*d*, *J* = 8.8 Hz, 1H), 7.90–7.86 (*t*, *J* = 7.6 Hz, 1H), 7.79–7.76 (*m*, 2H), 7.70–7.68 (*d*, *J* = 8.4 Hz, 3H), 7.64–7.58 (*m*, 2H), 7.57–7.55 (*dd*, *J* = 8.2, 1.8 Hz, 2H), 7.14–7.14 (*d*, *J* = 1.6 Hz, 2H), 6.53–6.51 (*d*, *J* = 8.8 Hz, 1H), 6.01 (*s*, 1H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 184.3, 153.4, 149.7, 143.4, 138.6, 137.7, 135.3, 133.8, 133.0, 132.2, 132.1, 131.3, 131.0, 130.8, 130.6, 128.1, 127.8, 127.5, 127.1, 126.5, 126.0, 125.5, 124.2, 123.9, 122.8, 122.1, 57.3. Anal. Calcd for C₃₃H₁₇Br₂NO: C, 65.95; H, 2.85; N, 2.33. Found: C, 65.92; H, 2.86; N, 2.35.

(5) (Z)-4-(Naphthalen-1-ylimino)naphthalen-1(4H)-one (NINO, **2e**). This compound was prepared following the general procedures by applying **1e** (0.538 g, 2 mmol) to give **2e** (0.463 g, 1.64 mmol) as a red solid with the yield of 82%. GC-MS (EI-*m/z*) calcd for C₂₀H₁₃NO⁺ [*M*]⁺ 283.10, found 282.95. ¹H NMR (400 MHz, CDCl₃, ppm): δ 8.68–8.66 (*d*, *J* = 8.4 Hz, 1H), 8.23–8.21 (*d*, *J* = 7.6 Hz, 1H), 7.91–7.88 (*d*, *J* = 8.8 Hz, 2H), 7.83–7.79 (*t*, *J* = 7.6 Hz, 1H), 7.75–7.73 (*d*, *J* = 8.0 Hz, 2H), 7.57–7.53 (*t*, *J* = 7.6 Hz, 1H), 7.51–7.47 (*t*, *J* = 7.8 Hz, 2H), 7.26–7.23 (*d*, *J* = 10.4 Hz, 1H), 6.79–6.78 (*d*, *J* = 7.2 Hz, 1H), 6.69–6.66 (*d*, *J* = 10.4 Hz, 1H). ¹³H NMR (100 MHz, CDCl₃, ppm): δ 185.6, 155.4, 146.2, 134.7, 134.1, 134.0, 133.1, 131.4, 131.4, 130.5, 127.9, 127.1, 126.7, 126.2, 126.1, 125.7, 125.5, 124.0, 114.7. Anal. Calcd for C₂₀H₁₃NO: C, 84.78; H, 4.63; N, 4.94. Found: C, 84.95; H, 4.59; N, 4.82.

TABLE 1: Optimization of the reaction conditions^a.

Entry	Solvent	Irradiation	Gas	Time (h)	Yield (%) ^b

1	CCl ₄	UV lamp ^c	Air	24	40 ^d
2	CCl ₄	Sunlight	Air	6	82 ^d
3	Acetone	Sunlight	Air	6	76
4	MeOH	Sunlight	Air	6	30
5	THF	Sunlight	Air	6	10
6	DMF	Sunlight	Air	6	20
7	Toluene	Sunlight	Air	6	50
8	MeCN	Sunlight	Air	6	78
9 ^e	MeCN	Dark	Air	6	nr
10	MeCN	Sunlight	O ₂	3	83
11	MeCN	Sunlight	N ₂	6	nr

^aReactions were carried out with **1a** (2.0 mmol) in solvent (400 mL) for 6 h.

^bIsolated yields. ^c365 nm. ^dWith isolated yield of **2b**. ^eAt 80°C.

(6) 5H-spiro[dibenzo[*c,h*]acridine-7,9'-fluorene]-5,6(14H)-dione (SFDBAOO, **3**). This compound was prepared following the general procedures by applying **1a** (0.862 g, 2 mmol) and acetone as solvent to give **3** (0.085 g, 0.184 mmol) as a red solid with the yield of 9%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.23–9.21 (*d*, *J* = 8.0 Hz, 1H), 9.18–9.16 (*d*, *J* = 8.0 Hz, 1H), 8.19–8.17 (*d*, *J* = 8.0 Hz, 1H), 7.93–7.87 (*m*, 3H), 7.74–7.66 (*m*, 3H), 7.57–7.53 (*m*, 1H), 7.44–7.40 (*m*, 3H), 7.21–7.17 (*t*, *J* = 7.6 Hz, 2H), 7.11–7.09 (*d*, *J* = 7.6 Hz, 2H), 7.03 (*s*, 1H), 6.40–6.38 (*d*, *J* = 8.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 179.4, 150.6, 149.7, 149.5, 142.0, 137.4, 136.2, 133.6, 133.3, 132.0, 130.4, 129.6, 128.8, 128.3, 128.0, 127.6, 127.6, 127.0, 126.6, 126.1, 126.0, 124.8, 124.5, 123.8, 119.9, 116.1, 54.9. MALDI-TOF-MS calcd for C₃₃H₁₉NO₂: 461.49 [*M*]⁺, Found: 462.14.

2.2.2. Syntheses of 2-(Thiophen-2-yl)-spiro [Fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one (TSFDBAO). A mixture of **2c** (0.523 g, 1.0 mmol), 2-thiopheneboronic acid **4** (0.154 g, 1.2 mmol), Pd(PPh₃)₄ (122 mg, 0.10 mmol), K₂CO₃ (2.0 M aqueous solution, 3.5 mL), and toluene (5 mL)/THF (5 mL) was stirred at 90°C under nitrogen atmosphere for 24 h. After it was cooled to room temperature, 200 mL of CH₂Cl₂ was added to the reaction mixture. The organic portion was separated and washed with brine before dried over anhydrous MgSO₄. The solvent was evaporated off, and the solid residues were purified by flash column chromatography using CH₂Cl₂: petroleum ether = 1 : 3 to afford TSFDBAO (0.437 g, 0.83 mmol) as red solids with the yield of 83%. ¹H NMR (400 MHz, CDCl₃, ppm): δ 9.29–9.27 (*d*, *J* = 8.4 Hz, 1H), 9.08–9.05 (*d*, *J* = 8.4 Hz, 1H), 8.14–8.12 (*d*, *J* = 8.4 Hz, 1H), 7.87–7.83 (*m*, 3H), 7.78–7.75 (*t*, *J* = 8.0 Hz, 2H), 7.71–7.69 (*d*, *J* = 7.2 Hz, 1H), 7.69–7.66 (*t*, *J* = 8.4 Hz, 1H), 7.61–7.57 (*t*, *J* = 8.4 Hz, 1H), 7.57–7.55 (*d*, *J* = 8.4 Hz, 1H), 7.43–7.39 (*t*, *J* = 8.0 Hz, 1H), 7.25 (*s*, 1H), 7.19–7.17 (*d*, *J* = 7.6 Hz, 1H), 7.17–7.15 (*m*, 2H),

FIGURE 2: Single-crystal X-ray structures of **2b** and **3** and the packing structure of **2b**.

7.00–6.98 (*d*, *J* = 7.6 Hz, 1H), 6.97–6.95 (*m*, 1H), 6.62–6.60 (*d*, *J* = 8.4 Hz, 1H), 6.09 (*s*, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 184.5, 152.5, 152.2, 149.9, 145.0, 143.6, 140.3, 140.0, 137.8, 135.6, 135.2, 133.7, 132.8, 132.2, 131.4, 130.8, 130.5, 130.4, 128.9, 128.7, 128.5, 128.0, 127.8, 127.3, 126.8, 126.7, 126.0, 125.3, 125.1, 124.7, 124.7, 123.8, 123.5, 122.2, 121.1, 120.7, 57.7. Anal. Calcd for $\text{C}_{37}\text{H}_{21}\text{NOS}$: C, 84.30; H, 4.02; N, 2.66. Found: C, 84.32; H, 4.01; N, 2.68.

2.2.3. Syntheses of 2,7-Di(thiophen-2-yl)-spiro [Fluorene-9,7'-dibenzo[*c,h*]acridine]-5'-one (DTSFDBAO). A mixture of **2d** (0.60 g, 1.0 mmol), 2-thiopheneboronic acid **4** (0.282 g, 3.0 mmol), $\text{Pd}(\text{PPh}_3)_4$ (245 mL, 0.20 mmol), K_2CO_3 (2.0 M aqueous solution, 7.2 mL), and toluene (5 mL)/THF (5 mL) was stirred at 90°C under nitrogen atmosphere for 24 h. After it was cooled to room temperature, 200 mL of CH_2Cl_2 was added to the reaction mixture. The organic portion was separated and washed with brine before dried over anhydrous MgSO_4 . The solvent was evaporated off, and the solid residues were purified by flash column chromatography using CH_2Cl_2 :petroleum ether = 1:3 to afford DTSFDBAO (0.487 g, 0.80 mmol) as red solids with the yield of 80%. ^1H NMR (400 MHz, CDCl_3 , ppm): δ 9.31–9.29 (*d*, *J* = 8.4 Hz, 1H), 9.09–9.07 (*d*, *J* = 8.4 Hz, 1H), 8.14–8.12 (*d*, *J* = 7.6 Hz, 1H), 7.90–7.84 (*m*, 3H), 7.80–7.60 (*t*, *J* = 8.0 Hz, 2H), 7.70–7.67 (*m*, 3H), 7.62–7.56 (*m*, 2H), 7.20–7.20 (*d*, *J* = 1.6 Hz, 2H), 7.19–7.18 (*d*, *J* = 5.2 Hz, 2H), 7.16–7.15 (*d*, *J* = 3.6 Hz, 2H), 6.97–6.94 (*m*, 2H), 6.66–6.64 (*d*, *J* = 8.4 Hz, 1H), 6.13 (*s*, 1H). ^{13}C NMR (100 MHz, CDCl_3 , ppm): δ 184.5,

SCHEME 2: Scope of the iminoquinones. ^aReactions were carried out with **1** (2.0 mmol) in MeCN (400 mL) for 6 h. ^bIsolated yields.

153.1, 149.9, 144.7, 143.6, 139.5, 137.7, 135.5, 135.2, 133.7, 132.8, 132.2, 131.4, 130.9, 130.5, 128.1, 128.0, 127.8, 127.3, 126.9, 126.7, 126.0, 125.4, 125.1, 124.8, 123.8, 123.6, 122.0, 121.1, 57.5. Anal. Calcd for $\text{C}_{41}\text{H}_{23}\text{NOS}_2$: C, 80.84; H, 3.81; N, 2.30. Found: C, 80.86; H, 3.82; N, 2.28.

3. Results and Discussion

Initially, our explorations toward an photooxygenation protocol under mild reaction conditions focused on the

FIGURE 3: (a) The absorption spectra of SFDBA and SFDBAO. Absorption spectra of **1a** at different reaction times: (b) under the sunlight, (c) under the 365 nm UV lamp, and (d) under 490 nm UV lamp.

reaction of 14H-spiro- [dibenzo[c,h]acridine-7,9'-fluorene] (SFDBA, **1a**) (Table 1). First, the reaction of **1a** was purposively carried out in CCl_4 by exposure to UV irradiation of 365 nm for 24 h, giving the chloro-substituted oxidative product (CISFDBAO) **2b** in 40% yield, whereas the SFDBAO product **2a** was not observed (entry 1). The structure of **2b** was confirmed unambiguously by X-ray single-crystal diffraction (Figure 2). It is exciting that the conversion yield of **2b** was improved up to 82% by exposure to sunlight at room temperature in CCl_4 (entry 2). A possible mechanism for the

formation of CISFDBAO (**2b**) is depicted in Figure S6 (see Supplementary Materials). When acetone was used as the solvent and conducted at room temperature, the desired product (SFDBAO) **2a** was obtained in 76% yield, and 9% of 5H-spiro[dibenzo[c,h] acridine-7,9'-fluorene]-5,6(14H)-dione (SFDBAOO) **3** as a by-product was detected (entry 3). The structure of **3** was confirmed unambiguously by X-ray single-crystal diffraction (Figure 2). Solvent screening indicates that MeCN was the most efficient. Other solvents such as, MeOH, THF, DMF, and toluene gave relatively low

SCHEME 3: The proposed triplet sensitization mechanism.

SCHEME 4: Synthesis of the thiophene-substituted SFDBAO D-A (*p-n*)-type organic semiconductors.

yields of **2a** (entries 4–8). No target compound **2a** was obtained in the dark when heating up more than 80°C (entry 9). Additionally, no product **2a** was obtained in N₂ atmosphere (entry 11), indicating oxygen in the atmosphere participated in the visible-light-mediated photooxygenation of **1a**. This result was further supported by the control experiments using the purified O₂ source to give **2a** in 83% yield (entry 10). Moreover, a write-once, read-many (WORM) type memory device based on SFDBAO derivative nanosheets as electroactive layers shows an ON/OFF ratio of 6.0×10^4 , accompanied by an interesting photoswitching behavior. The results presented have shown that SFDBAO derivatives are promising electroactive materials for the memory device application [22, 23]. Compared with our previous reports, further

study of the conditions and the scope of this reaction were conducted in detail.

Under the optimized conditions (Table 1, entry 8), a range of reactions were performed with various substrates **1** (Scheme 2). The reactions of spirofluoreneacridines proceeded smoothly to afford the corresponding photooxygenation products **2(a–d)** in good to excellent yields (70–82%). Then, di(naphthalen-1-yl) amine was compatible with this reaction, affording the desired product **2e** in 82% yields. To our disappointment, no desired products were obtained when naphthylamine and anilines were employed in the present reaction system (see Supplementary Materials Figure S6).

Chemical structures of the SFDBAO derivatives were unambiguously confirmed by GC-MS, ¹H and ¹³C NMR,

FIGURE 4: The photophysical and electrochemical properties of SFDBAO. (a) UV-vis electronic absorption spectra and photoluminescence spectra. (b) Reductive and oxidative cyclic voltammograms, 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in THF (reduction) and 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in CH_2Cl_2 (oxidation), were used as supporting electrolytes. A platinum sheet electrode was used as the working electrode; the scanning rate was 100 mV/s, where E^+ (Fc/Fc) is about 0.03 V.

X-ray crystallography, and elementary analyses. The single-crystal X-ray diffraction structures of ClSFDBAO (**2b**) and SFDBAO (**3**) are shown in Figure S3–S5 and Table S1. ClSFDBAO and SFDBAO from a mixture of dichloromethane/alcohol and a mixture idines in ClSFDBAO are incompletely perpendicular with fluorene plane according to X-ray crystallography, obviously different from spirobi-fluorenes. ClSFDBAO exhibit well-defined consecutive intermolecular π -stacked motifs among adjacent dibenzoacridines with a close distance of 3.346 Å in the molecular packing graph (Figure 2), which is in the range of the distance of the typical π - π stacking interactions relative to range over 3.4–3.8 Å. The closely interplanar distances are favorable for the electron delocalization and the improvement of mobility in organic films and devices.

To clarify the SFDBA and SFDBAO together as a photosensitive catalyst involved in the reaction leading to SFDBAO, control experiments were performed (Figure 3). The optical absorption properties of the SFDBA and SFDBAO were investigated by UV-vis absorption spectra as shown in Figure 3. The absorption spectra in dilute CHCl_3 of SFDBA and SFDBAO show absorption at 370 nm and 470 nm, respectively. Therefore, we tested the absorption spectra of SFDBA **1a** at different reaction times under the sunlight, the 365 nm UV lamp, and the 490 nm UV lamp, respectively. As a result, we found that the yield of SFDBAO increased gradually with the increase of reaction time under the sunlight and 490 nm UV lamp. However, the yield of SFDBAO increased very slowly with the increase of reaction time under the 365 nm UV lamp. The experimental results indicate that SFDBA acts as a photosensitive catalyst to induce the formation of SFDBAO in the initial reaction period, and then, SFDBAO also acts as another photosensitive catalyst accelerating the conversion together with SFDBA.

On the basis of all the results described above, a plausible and preliminary mechanism has been proposed, as depicted in Scheme 3. In the self-sensitizations cycle, naphthylamines is converted to the excited singlet state under the sunlight irradiation. Subsequently, the excited triplet singlet state is formed through intramolecular intersystem crossing (ISC) of the excited singlet state. The triplet energy of the naphthylamines can be transferred to the ground state oxygen molecule to produce singlet oxygen to close this catalytic cycle. After that, an electron transfer of singlet oxygen from **1** occurs, leading to the formation of radical cation species **I/II**. Then, a [4 + 2] cycloaddition is given to intermediate **II**, and the O–O bond cleavage of intermediate **III** led to intermediate **IV**, which was readily oxidized by dioxygen to produce the desired iminoquinones **2** [24–26].

In order to explore the photoelectric property of *n*-type spiro-based organic semiconductors SFDBAO, we smoothly synthesized the thiophene-substituted SFDBAO D-A (*p-n*)-type organic semiconductors, which will become important monomers for low-bandgap π -conjugated polymers in solar cells (Scheme 4). The reactions of **2c** and **2d** with thiophen-2-ylboronic acid **4** under $\text{Pd}(\text{PPh}_3)_4$ catalytic conditions gave 2'-(thiophen-2-yl)-5*H*-spiro[dibenzo[*c,h*]acridine-7,9'-fluoren]-5-one (TSFDBAO) and 2',7'-(thiophen-2-yl)-5*H*-spiro[dibenzo[*c,h*]acridine-7,9'-fluoren]-5-one (DTSFDBAO) in 83% and 80% yields, respectively.

The optical and electrochemical properties of the SFDBAO, TSFDBAO, and DTSFDBAO were investigated by UV-vis absorption spectra, photoluminescence (PL) spectra, and cyclic voltammetry (CV), as shown in Figure 4 and summarized in Table S2 (see Supplementary Materials). UV-vis spectra exhibit the maximum absorption peak at 470 nm for SFDBAO. SFDBAO with a red-yellow color about 565 nm. Thiophene-substituted SFDBAO exhibit the new

electronic absorption bands at 322 nm for TSFDBAO and 353 nm for DTSFDBAO without the obvious change of PL peaks, expect for the reduced emission intensity probably owing to heavy atom effects of sulfur. The first turn-on oxidation potentials of SFDBAO occur at 0.98 V (vs Fe^+/Fe) for SFDBAO, 0.96 V (vs Fe^+/Fe) for TSFDBAO, and 0.71 V for DTSFDBAO, respectively. These results indicate that DTSFDBAO has better electron-donating properties owing to the introduction of the double thiophene groups. Furthermore, all the SFDBAO derivatives exhibit the reversible reduction processes with the similar onset first potential of around -1.00 V (vs Fe^+/Fe). Their LUMO energy levels are estimated and determined from the onset of the reduction to be -3.73 eV for SFDBAO, -3.78 eV for TSFDBAO, and -3.77 eV for DTSFDBAO with regard to the energy level of ferrocene (4.8 eV below vacuum), respectively. The lower LUMO is probably assigned to the spiro-dibenzoacridine moieties with the electron-withdrawing properties, which are in the range of the LUMO energy level of acceptor material in solar cells [27, 28]. Their bandgaps are 2.02 eV for SFDBAO, 1.95 V for TSFDBAO, and 1.71 V for DTSFDBAO, respectively. These data suggest that the SFDBAOs are potential *n*-type green organic semiconductors.

4. Conclusions

We have developed a green efficient access to iminoquinones from naphthylamines based on the photooxygenation and self-sensitizations, in which naphthylamines play a dual role of providing both photosensitizer and substrate, and O_2 functions as triplet state trapping agent and oxygen source. Air atmosphere and sunlight irradiations are crucial conditions of the photooxygenation reaction to obtain the high-yield products. This sunlight-induced C-H activation gives a kind of new *n*-type spiro-based organic semiconductors. Further work on the application of SFDBAO-based materials is ongoing in our laboratory.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

Ying Wei and Lei Tang authors contributed equally.

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Supplementary Materials

2–4 p.: general procedure for synthesis and analytical data of spiro[fluorene-9,7'-dibenzo[*c,h*]acridine] (**1a**) and its derivatives of 2-bromospiro[fluorene-9,7'-dibenzo[*c,h*]acridine] (**1c**), 2,7-dibromospiro[fluorene-9,7'-dibenzo[*c,h*]acridine] (**1d**), and di(naphthalen-1-yl)amine (**1e**). 4 p.: Figure S1: photograph about this green reaction in different reaction times in sunlight: SFDBA **1a** in acetone solution ($0.005 \text{ mol} \cdot \text{L}^{-1}$). (a) 0 min; (b) 10 min; (c) 3 h. 5 p.: Figure S2: photographs of the color and emission change of reaction solution of SFDBA **1a** in the various solvents ($0.005 \text{ mol} \cdot \text{L}^{-1}$). (a) Before exposure to sunlight and shooting in daylight. (b) Before exposure to sunlight and shooting under UV lamp at 365 nm. From left to right the solvents are MeOH, THF, DMF, acetone, CHCl_3 , toluene, and acetonitrile. 6–7 p.: the crystal data of **2b** and **3**, 8 p.: Figure S6: GC-MS of the crude product of **2f**, and Figure S7: MALDI-TOF-MS of **3**. 9–20 p.: ^1H and ^{13}C NMR spectra of products. 21 p.: ^1H -NMR and ^{13}C -NMR spectra of DTSFDBAO. CCDC 802655(2b) and 1821185(3) contain the supplementary crystallographic data for this paper, and the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. (*Supplementary Materials*)

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