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Solution-Processable Core-Extended Quinacridone Derivatives with Intact Hydrogen Bonds

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S *Supporting Information*

ABSTRACT: A highly efficient and feasible "condensation followed by annulation" synthetic approach was developed to afford a subset of 9-ring-fused quinacridone derivatives on a 10 g scale. Despite the amenable intermolecular hydrogen-bonding ability of these rigid molecules, good solubility in common organic solvents and solution processability into uniformed thin films were achieved. Integrated advantages in the synthesis and properties make these compounds ideal building blocks for high-performance dyes and optoelectronic materials.

As a highly stable, red-colored pigment, quinacridone (Figure 1) was first synthesized 100 years ago.[1] Since the 1950s, the ink and pigment industry have been producing and using quinacridone and its derivatives extensively,[2] taking advantage of their vivid color, exceptional weather fastness, excellent environmental stability, low toxicity, and ability to be mass-produced. Similar to many other conventional pigments such as perylene diimide[3] and isoindigo,[4] quinacridone has attracted significant research attention from organic electronics and photovoltaics communities in the past few years.[5] It has been demonstrated that quinacridone could serve as a promising building block for optoelectronic applications due to its high charge carrier mobility in field-effect transistor devices[5a] ($\mu_h = 0.2$, $\mu_e = 0.01$ cm^2 V^{-1} s^{-1}) and promising attributes as active materials for organic solar cells.[5d,f,g,6] Quinacridone derivatives also showed high photoluminescent efficiencies and excellent electrochemical stabilities and were thus useful for organic light-emitting materials.[5e,7]

The H-bonding ability plays a pivotal role in governing the materials' properties of quinacridone.[5a,8] On the rigid backbone, two sets of carbonyl and N−H functions are organized in a centrosymmetrical manner, so that a pair of strong and complementary hydrogen-bonds (H-bonds) can be formed intermolecularly. These H-bonding interactions not only guide the solid-state packing mode of quinacridone derivatives but also lead to their high thermal, chemical, and photochemical stability.[5a,8] Unfortunately, such a strong intermolecular interaction often also deteriorates the solubility and solution processability of most H-bond-containing quinacridone derivatives. In contrast, one of the most efficient ways to solubilize a quinacridone derivative was converting the N−H H-bond donors at the N5/12 positions into *N*-alkylated groups.[9] However, the fascinating property features brought about by H-bonds were diminished at the same time. Therefore, it is an intriguing challenge to synthesize solution-processable quinacridone derivatives while maintaining their H-bonding ability.[5b]

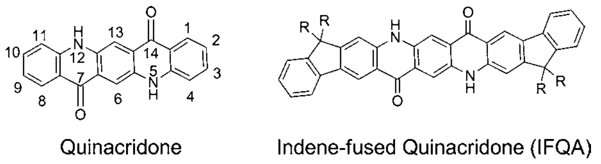

Figure 1. Structural formula of quinacridone and IFQA.

From a synthetic perspective, there is still an ongoing demand for a scalable and industry-friendly approach to the production of quinacridone derivatives. So far, annulation of the quinacridone core requires either reflux in high boiling point solvents (Dowtherm A or α-chloronaphthalene)[5e,10] or treatment with hot concentrated acids.[11] These harsh conditions limited the choice of substrate and also increased the cost for mass production. In addition, toxic oxidants (e.g., nitrobenzene or chloranil)[10] were often required, resulting in severe negative impact on the environment during the mass production of quinacridone compounds.

Addressing both aforementioned challenges together, we report a scalable and facile synthesis that affords solution-processable quinacridone derivatives with intact H-bonding ability. To achieve this goal, we designed a unique synthetic target—core-extended indene-fused quinacridone (IFQA, Figure 1). On this 9-ring-fused backbone, solubilizing alkyl chains can be easily installed on the bridging sp^3 positions of the indene component rather than on the nitrogen atoms in the central quinacridone core. The H-bond-donating feature of the N−H group can therefore be retained. In terms of cost, the main starting material of IFQA (i.e., fluorene) is an inexpensive, mass-

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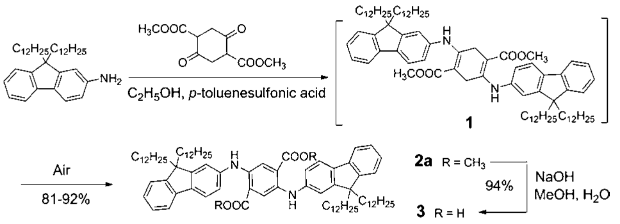
produced commodity chemical as a byproduct of the coke industry.[12] Taking advantage of the good solubility and high regioselectivity of fluorene starting materials, we developed a cost-effective and environmentally benign synthetic route, "condensation followed by annulation", for general construction of soluble quinacridone derivatives.

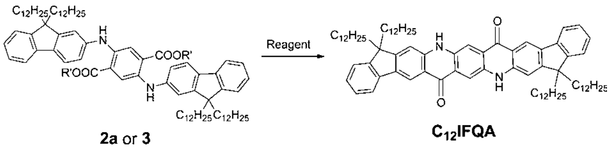
The synthetic route of IFQA began (Scheme 1) with imine condensation between 2-amino-9,9-dialkylfluorene and dimethylsuccinyl succinate (DMSS) in a 2:1 stoichiometric ratio, which led to intermediate **1**. Surprisingly, the central cyclohexadiene ring of **1** can be quantitatively oxidized into the benzene ring in situ by air.[13] As a result, the desired aniline derivative **2a** could be prepared in one pot without the addition of any toxic oxidant, marking a significant improvement over conventional methods.

Scheme 1. One-Pot Synthesis of Intermediates 2a Followed by Hydrolysis to 3



To optimize the subsequent annulation reaction, dodecyl-functionalized **2a** was selected as the model compound for the condition screening. Ester groups in **2a** were first hydrolyzed by NaOH in methanol to give dicarboxylic acid **3**. The annulation reaction of **3** relied on heat or acid-promoted electrophilic aromatic substitution between the fluorene moieties and the carboxylic acid groups (Table 1). In preliminary tests, no reaction was observed in thermal conditions such as refluxing in α-chloronaphthalene at 263 °C. Conventional acidic conditions, such as polyphosphoric acid (PPA),[11] Eaton's reagent, and concentrated sulfuric acid, all afforded yields lower than 40% and gave a large amount of polar byproducts, which were likely formed by undesired introduction of sulfonate or phosphonate groups onto the aromatic backbone. The best condition was found to be heating at 120 °C in pure methanesulfonic acid (MSA), giving an 84% isolated yield and no polar byproduct. It should also be noted that this condition resulted in only the linear IFQA without the formation of its angular-shaped regioisomer,[14] showing the high regioselectivity of fluorene unit as a Friedel–Crafts nucleophile.

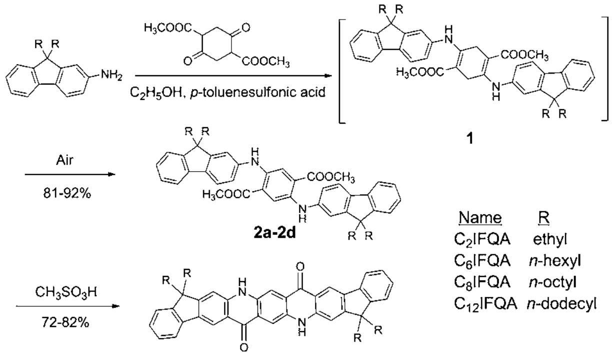
Table 1. Optimization of the Ring Annulation Reaction Conditions[a]



entry	R′	reagent	temp (°C)	yield (%)[b]
1	H	α-chloronaphthalene	263	0
2	H	PPA	140	18
3	H	PPA + silica gel[c]	140	35
4	H	Eaton's reagent	140	38
5	H	H_2SO_4	140	0
6	H	CH_3SO_3H[d]	120	84
7	CH_3	CH_3SO_3H[d]	140	82

[a] Reaction conditions: 10 equiv of reagent (v/w), 24 h. [b] Isolated yield. [c] Dispersed on silica gel and mixed with PPA. [d] Reaction was conducted for 12 h.

Scheme 2. Optimized Two-Step "Condensation Followed by Annulation" Synthetic Route to C_nIFQA



Name	R
C_2IFQA	ethyl
C_6IFQA	n-hexyl
C_8IFQA	n-octyl
C_{12}IFQA	n-dodecyl

Further optimization revealed that diester precursor **2a** could also be directly annulated in MSA to afford the final IFQA product. Although the yield (82%) was slightly lower than that from **3**, this strategy allowed for skipping the hydrolysis step, making the synthesis of IFQA a concise two-step route with an overall yield of ~75%. A series of IFQA derivatives (C_nIFQA) with ethyl (C_2), hexyl (C_6), octyl (C_8), and dodecyl (C_{12}) side chains were synthesized on up to a 10 g scale using this "condensation followed by annulation" method (Scheme 2). All intermediates and products were fully characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry. ^{1}H–^{1}H COSY and NOESY NMR spectra were recorded to fully elucidate the structure and to unambiguously assign the resonance peaks (see the Supporting Information). Thermogravimetric analysis of C_nIFQA showed a clear weight loss in the range of 400–480 °C, corresponding to the decomposition of the alkyl groups. Carbonization yield at 600 °C agreed well with the theoretical percentage of the quinacridone backbone in each compound (see the Supporting Information). All C_nIFQA derivatives were soluble in mixed solvents such as chloroform/ethanol, hexane/ethanol, toluene/DMSO. With longer dodecyl chains grafted, C_{12}IFQA was even soluble in hexane or heptane up to 1.5 mg/mL. The good solubility of C_nIFQA paved the way for their solution-phase characterization and solution processing.

This novel "condensation followed by annulation" method is particularly suitable for large-scale synthesis of quinacridone derivatives. Compared to the prevailing three-step synthetic routes of quinacridone that often require toxic oxidants and high boiling point solvents,[2b−d,5e,10a] this method involved only two highly efficient steps from aromatic amine and DMSS. Furthermore, the products can be easily purified by recrystallization without chromatography. Such a simplified procedure would reduce the cost dramatically for potential mass production. Finally, both reaction solvents (ethanol and MSA[15]) used in this procedure were low cost, nontoxic, and had minimal environmental impact.

To investigate the H-bonding property, concentration-dependent and variable-temperature ^{1}H NMR spectra of C_{12}IFQA were recorded in $CDCl_3$ (Figure 2). Either when the concentration was decreased or when the temperature was increased, the characteristic ^{1}H NMR resonance peak for the N–H group shifted upfield, indicating the dissociation of the H-

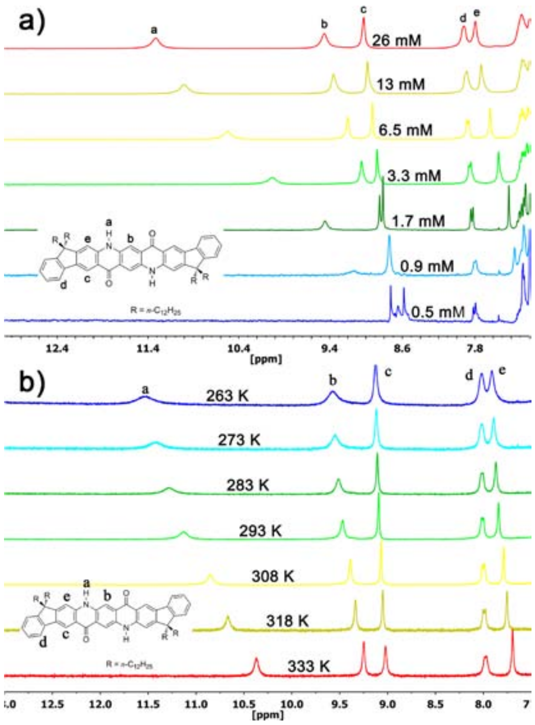


Figure 2. (a) Room temperature variable concentration and (b) variable-temperature ^{1}H NMR spectra of C_{12}IFQA in $CDCl_3$.

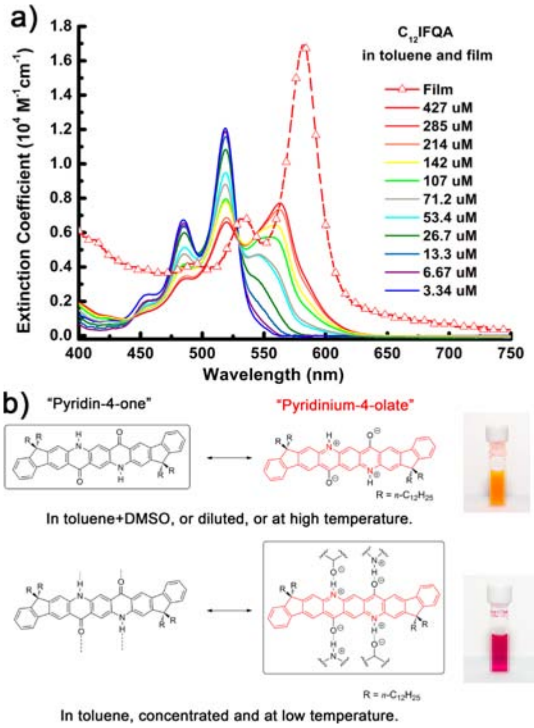


Figure 3. (a) Concentration-dependent UV−vis spectra of C_{12}IFQA in toluene and in the thin film state at room temperature. Solution spectra are in absolute molar absorption coefficient. The thin film spectrum was normalized based on the isosbestic saddle point. (b) Schematic diagram describing the impact of H-bonds on the resonance contribution of C_{12}IFQA with the predominant species encircled. Corresponding photographic images of the solution are shown.

bonds under these conditions.[16] Concentration-dependent UV−vis absorption spectra of C_{12}IFQA were recorded (Figure 3a) in toluene. At low concentration (<5 μmol/L), the absorption λ_{max} was at 518 nm with two additional characteristic vibrational progression peaks at 484 and 455 nm. After the concentration was increased, a red-shifted absorption band with λ_{max} = 565 nm emerged. This change in absorption originated from the alternated resonance contribution of IFQA molecules induced by H-bonds (Figure 3b). When the H-bond was not formed, the resonance form of "pyridine-4-one" dominated in discrete IFQA molecules. With the intermolecular H-bonds, the "pyridinium-4-olate" resonance form, however, became more favorable because of the change in N−H acidity and C═O bond strength.[17] The clear isosbestic point at 526 nm indicated that the absorption was caused by only two distinctive species—isolated IFQA and H-bonded IFQA, which were related linearly by stoichiometry.[10a,18] Based on the variable concentration UV−vis spectra, free Gibbs energy change ($\Delta G°$) for the H-bonded association of each C_{12}IFQA molecule was estimated to be −4.5 kcal/mol using an isodesmic aggregation model (see the Supporting Information).[19] This value matched well with the strength of a typical N−H-involved H-bond (1.9−3.1 kcal/mol for each H-bond).[20] It should be noted that $\pi-\pi$ stacking interaction of IFQA was not taken into account in this solution-phase investigation because the corresponding $\Delta G°$ magnitude was estimated[21] to be <1 kcal mol^{-1} at 298 K on an *N*-alkylated quinacridone derivative. Upon the addition of a H-bond competing solvent such as DMSO into the concentrated solution, as expected, the spectrum revolved back to the shape of a diluted solution, as a result of competitive dissociation of intermolecular H-bonds (see the Supporting Information). A clear self-quenching of fluorescent emission was also observed while increasing the concentration of C_{12}IFQA in solution, as a result of the intermolecular aggregation (see the Supporting Information). Solid-state UV−vis spectrum of C_{12}IFQA was similar to that in concentrated nonpolar solvent (Figure 3a), except that the spectrum was slightly further red-shifted, indicating a complete H-bonded form and possible $\pi-\pi$ stacking interaction in the thin film. These experimental results unambiguously confirmed the H-bonding ability of C_{12}IFQA in solution and in the solid state. The same phenomena were also observed for C_8IFQA (see the Supporting Information).

IFQA derivatives can be easily processed into uniform thin films, due to their good solubility in common organic solvents. For example, C_8IFQA thin film was spin-cast for a general morphological investigation. The thin film showed good uniformity under an optical microscope and an atomic force microscope (AFM). According to AFM (Figure 4), the root mean square (rms) roughness of the film was 0.31 nm. After being annealed, the film remained uniform with a slightly higher rms of 0.73 nm. The excellent film-forming ability of the compound enabled the preparation of homogeneous and stable

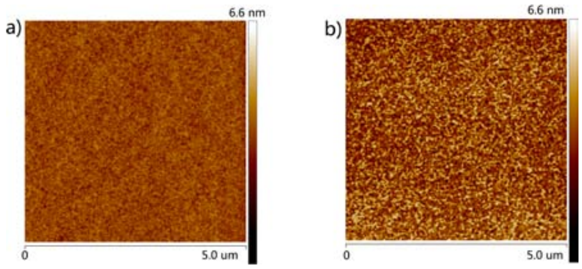


Figure 4. AFM images (5 × 5 μm) of C_8IFQA thin film prepared by spin-coating method (a) before and (b) after thermal annealing at 210 °C.

thin films from solution, allowing for future investigation of their properties and for application in thin film devices, including charge carrier mobility, exciton diffusion length, and thermal conductivity.

In conclusion, a series of core-extended quinacridone derivatives with intact H-bonds were synthesized by a novel “condensation followed by annulation” strategy. This highly efficient, environmentally benign, and cost-effective route enabled the preparation of these soluble quinacridone-derived materials in large scale. Their H-bonding ability was confirmed by solution-phase ^{1}H NMR and UV−vis spectroscopy experiments. Uniform films can be easily cast by spin-coating. Facile synthesis and unique combination of properties of IFQA derivatives render them promising building blocks for the construction of materials for high-performance dyes and optoelectronic devices.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details (synthesis and characterization) and NMR spectra of all new compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01465.

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Notes

The authors declare no competing financial interest.

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