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1. Introduction

Organic semiconductors with both high mobility and strong solid fluorescence are highly pursued for the development of emerging organic optoelectronic devices such as organic lightemitting transistors (OLETs),¹ electrically driven organic lasers² and so on. However, it is a big challenge to develop these dual functional materials. Generally, achieving high mobility in

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A new type of solid-state luminescent 2-phenylbenzo[g]furo[2,3-b]quinoxaline derivative: synthesis, photophysical characterization and transporting properties[†]

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Organic semiconductors combining high mobility and efficient solid fluorescence are in high demand for developing organic light-emitting transistors and electrically driven organic lasers. But, achieving such dual functional molecules is extremely challenging. In this manuscript, we report 2-phenylbenzo[g]furo[2,3-b]-quinoxaline derivatives (**3a–3c**) and develop a new synthesis method for the furo[2,3-b]quinoxaline core. It was found that **3a** exhibited favorable aggregation induced emissive enhancement behavior and reasonable hole mobility. The absolute photoluminescence quantum yield of **3a** is determined to be 22.1% in solid powders and can reach a maximum of 19.7% in 50% water in THF, twice that in CH₂Cl₂ solution (9.2%) and dispersed in PS film (9.3%). The single crystal and thin film organic field-effect transistor of **3a** show a hole mobility of 2.58 × 10⁻² cm² V⁻¹ s⁻¹ and 5.7 × 10⁻³ cm² V⁻¹ s⁻¹, respectively. Our results demonstrated that the 2-phenyl-benzo[g]furo[2,3-b]quinoxaline skeleton is a promising candidate for building multifunctional organic optoelectronics.

organic semiconductors requires crystalline aggregation with strong π - π interactions,³ which most often lead to exciton quenching and thus luminescence suppression in the solid state.⁴ As a result, nearly all efficient electroluminescent organic molecules have been designed to have steric hindrance or a twisted structure in order to inhibit intermolecular interactions. On the contrary, organic semiconductors in organic field-effect transistors (OTFTs) were constructed to have flat, conjugated and rigid molecular structures so as to strengthen π - π interactions.⁵ Therefore, the combination of emission and mobility into one molecule seems to be a dilemma.

The linearly fused aromatic cores⁶ are one important family of organic semiconductors and show benchmark charge mobility. Recent research works by Perepichka⁷ and Hu *et al.*⁸ demonstrated that anthracene derivatives have dual functions. In single crystals of 2,6-diphenylanthracene, the hole mobility and photoluminescence quantum efficiency (PLQY) are as high as 34 cm² V⁻¹ s⁻¹ and 41.2%, respectively.^{8a} The authors subsequently demonstrated that single crystals of 2,6-di(2-naphthy)anthracene also afford charge transport up to 12.3 cm² V⁻¹ s⁻¹ and a PLQY of 29.2%.^{8b} These results inspired us to explore larger fused aromatic ring molecular systems to obtain such dual functional organic semiconductors. A larger fused aromatic core would give rise to better charge mobility.^{5b} The derivative of tetracene, rubrene, exhibits hole mobility as high as

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 \sim 40 cm² V⁻¹ s⁻¹ and a PLQY of nearly 100% in solution, but the solid state PLQY drops down to less than 1%.9 Recently, Zhen and Hu et al.10 realized the solid luminescence enhancement of rubrene analogues by substituting side or peripheral phenyl groups with thienyl groups. The aggregation-caused luminescence quenching of these larger polyacenes and their derivatives is usually considered to be a result of singlet fission, which is likely to occur when the number of fused aromatic rings is more than four due to the close energy between the singlet and two triplet excitons.¹¹ Another benchmark p-type semiconductor fused by four aromatic rings, 2,7-dioctyl[1]benzenothieno[3,2-b]-[1]benzothiophene, has a hole mobility of 43 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in film OTFTs, but does not exhibit fluorescence in the solid state.¹² The present progress indicates that it is greatly challenging for derivatives of larger polyacenes to combine both a high charge mobility and efficient solid fluorescence.

In this context, a benzo[g]furo[2,3-b]quinoxaline core substituted with phenyl and 4-alkyl-phenyl groups is designed as a new kind of promising dual functional semiconductor material synthesized by a one-pot cascade synthesis. The designed molecular framework is based on two considerations. First, furan and its derivative have been demonstrated to possess greater rigidity and show higher fluorescence in comparison to the corresponding thiophene analogues,¹³ but show comparable mobility to thiophene moieties due to the dense packing nature, resulting from a smaller element size.¹⁴ Secondly, introduction of N into acene would provide a chance for tuning the electronic structure, stability and molecular packing of heteroacenes.¹⁵ Thus, it is expected that the combination of furan with N-heteroacene could produce a new kind of semiconductor material with interesting properties. Encouragingly, the compound without an alkyl chain, 2-phenylbenzo[g]furo[2,3-b]quinoxaline, is prone to forming a needle crystal in solution, which provides a hole mobility of $2.58 \times 10^{-2} \mbox{ cm}^2 \mbox{ V}^{-1} \mbox{ s}^{-1}$ in normal single crystal OTFTs and a maximum PLQY of 22.1% in solid powders. While compounds with alkyl chains show a weak ability to self-assemble into crystals in solution, resulting in lower mobility, our results clearly demonstrated that benzo[g]furo[2,3-b]quinoxaline is a promising molecule building unit for developing a dual functional organic semiconductor and the introduction of an alkyl chain in this molecule structure can disturb the molecular ordered arrangement.

2. Results and discussion

2a. Synthesis

The chemical structure and the synthesis of phenyl and 4-alkylphenyl group substituted benzo[g]furo[2,3-b]quinoxaline 3a-3care shown in Scheme 1. Only a few literature methods have been reported for the synthesis of furo[2,3-b]quinoxaline,¹⁶ in which most of the methods involved transition metal catalyzed Sonogashira coupling of 2,3-dichloroquinoxalines with terminal alkynes, hydrolysis and subsequent cyclization steps.^{16e} Later, two-step and one-pot synthesis procedures of furo[2,3-b]quinoxaline were developed by Pal and co-workers^{16b} and Verma's group^{16d}



Scheme 1 Molecular structures of 3a-3c and their synthetic routes.

using similar substrates, respectively. In another way, Narender's group developed a microwave-assisted one-pot synthesis procedure of furo[2,3-*b*]quinoxalines using *o*-phenylenediamine, ethyl-glyoxalate, and terminal alkyne as substrates.^{16f} These procedures involved using transition metal catalytic agents. However, for a larger aromatic fused ring, the pre-functionalization of the starting materials becomes difficult. Certainly, simple and straightforward strategies involving readily available starting materials and low-cost catalysts are urgently required.

Here, we synthesized benzo[g]furo[2,3-b]quinoxaline 3a-3c using only low cost catalysts and solvent combinations of acetic acid and polyphosphoric acid through one-pot synthesis procedures. It was reported that 5-phenyl-2,3-dihydrofuran-2,3-dione reacting with 1,2-phenyldiamine in dioxane would result in the furan ringopened product, 3,4-dihydro-3-(2-oxo-2-phenylethylidene)-2(1H)guinoxalinone.¹⁷ Our initial attempt for the synthesis of 5-phenylbenzo[g]furo[2,3-b]quinoxaline was using a one-step procedure. To pursue our objective, we began our investigation using 2,3-naphthalenediamine and 5-phenyl-2,3-dihydrofuran-2,3-dione as model substrates with acetic acid as solvent and catalyst. It was found that 5-arylfuran-2,3-dione reacted with 2,3-naphthalenediamine in boiling acetic acid only to afford the furan ringopened intermediate 2. We then successfully implemented the cyclization of intermediate 2 with polyphosphoric acid and afforded the desired final products 3a-3c in high yields. Inspired by our preliminary results, we further explored the reaction of the sequential one-pot addition of polyphosphoric acid. Fortunately, the target products 3a-3c can also be successfully obtained in high yields in our previous two-step procedures when we add polyphosphoric acid to the reaction mixture of 5-phenyl-2,3-dihydrofuran-2,3-dione and 2,3-naphthalenediamine in acetic acid and reflux for about eight hours. We also successfully synthesized compounds 3b and 3c using this one-pot synthesis procedure or two-step procedures, respectively. We anticipate that this simple one-pot protocol will be useful for the synthesis of N-, O- and S-containing polycyclic heterocylic compounds.

2b. Steady state and transient optical properties

Fig. 1 shows the ultraviolet-visible absorption and photoluminescence (PL) spectra of 3a-3c in CH_2Cl_2 solution and solid powder form. The photophysical, electrochemical, and energy-level data for compounds 3a-3c are summarized in Table 1. The three compounds exhibit the same absorption and PL spectral shape in solution. This phenomenon implies



Fig. 1 UV-visible absorption and photoluminescence spectra of 5a-5c in CH_2Cl_2 solution and solid powders.

that the substitution of long alkyl chains has little effect on the UV and PL data of the resulting compounds in solution. Switching to solid powder samples, the absorption spectra of **3a–3c** show a bathochromic shift of about 20 nm with more vibronic splitting bands and an obviously enhanced 0–0 absorption peak. The bathochromic shift and the increasing ratio between the 0–0 and 0–1 peak intensity in the absorption spectra as compared with that in solution suggest a J-aggregated mode of the three compounds in the solid state. The blue-shift of the PL peak of compounds **3b** and **3c** as compared with that of **3a** indicates that although the introduction of an alkyl chain to 5-phenylbenzo[g]furo[2,3-b]quinoxaline makes a small contribution to tuning the photophysical properties of the resulting compounds in solution, it exerts a significant influence on molecule packing in the aggregation state.

The absolute PLQYs of **3a–3c** were measured using an integrating sphere and are shown in Table 1. In CH₂Cl₂ solution, the three compounds show comparable PLQYs with values of 9.2%, 8.0% and 12.3% for **3a**, **3b** and **3c**, respectively. But, their PLQY values in the solid state are significantly different. **3a** shows aggregation induced emission enhancement (AIEE). The PLQY of **3a** in solid powder form is 22.1%, twice that in CH₂Cl₂ solution (9.2%) and dispersed in PS film (9.3%). This PLQY value is higher than that of reported powder samples such as 1,5-, 2,6-, and 9,10-bis-[2-(4phentylphenyl)vinyl]anthracenes (4–22%),^{7a} and it is lower than the recently reported result of crystalline solids of 1,6- and 2,7*trans*- β -styryl pyrenes (28.8% and 27.4%).^{1d} The solid powders of **3b** show almost the same PLQY as that in solution. However, the

Table 1 Photophysical, electrochemical, and energy-level data for compounds ${\bf 3a-3c}$

	$\Phi_{ m F}{}^a$ /%	$\Phi_{ m F}{}^b/\%$	$E_{\rm g}/{\rm eV}$	IP	$E_{\rm LUMO}^{c}/{\rm eV}$	$E_{\rm HOMO}^{d}/eV$
3a	9.2	22.14	2.56	-5.58	-3.01	-5.57
3b	8.0	7.97	2.56	-5.47	-2.66	-5.22
3c	12.3	2.46	2.57	-5.51	-2.61	-5.18

^{*a*} Photoluminescence quantum yield in CH_2Cl_2 solution. ^{*b*} PLQY of powders. ^{*c*} Estimated as $E_{LUMO} = [-4.8 - E_{red}^{onset} vs. Fc/Fc^+] eV.$ ^{*d*} Obtained by using equation HOMO = LUMO - E_{c}^{opt} . PLQY of **3c** decreased from 12.3% in solution to 2.5% in the solid state. For crystalline samples, several factors influence the PLQY, such as chemical impurities, structural defects, re-absorption of fluorescence¹⁸ and so on. For the **3c** sample, the chemical impurities and structural defects may be mainly responsible for this profound decrease of PLQY while for **3a**, higher PLQYs (>22.1%) are expected in highly purified crystal-line samples.¹⁸

To understand this AIEE effect of 3a, we further measured the fluorescence spectra of 3a in different mixed ratios of THF/ H₂O, as shown in Fig. 2. With an increase of the water fraction in the range of 0–50%, the emission intensity increased with a significant red-shift. At 50% water fraction, the emission intensity reached a maximum value with a PLQY of 19.7%, two times that in the pure THF solvent.

In order to clarify the excited state dynamics of the new compounds, time-resolved photoluminescence and femtosecond transient absorption (TA) spectroscopy at room temperature were measured. Fig. 3a and c depict the TA spectra of **3a** and **3b** at various time delays upon excitation at 380 nm and Fig. 3b and d show the kinetic traces of the two compounds for different probe wavelengths. It is clear that the excited state (ES) absorption of both compounds was mainly governed by a strong broad peak (P-I) in the green region. In addition, two weak peaks were observed in the blue (P-II) and red (P-III) regions, respectively. For **3a**, the P-I band centered at 525 nm shows initial



Fig. 2 (a) Photographs of **3a** with different water contents and (b) PL spectra of **3a** $(1 \times 10^{-5} \text{ M})$ in a H₂O–THF mixture with varying water fractions.



Fig. 3 Transient absorption spectrum data at different delay times for (a) **3a** and (c) **3b**; kinetic traces with different probe wavelengths for (b) **3a** and (d) **3b**.

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absorption at the delay time of about 0.107 ps and a continuous growth in intensity before 139 ps. The kinetic trace of this band shows a rapid increase in the initial 27 ps and then a decrease in the subsequent delay time till 5.7 ns. The former rapid increase is ascribed to the vibration relaxation process of the excited state. Thus, this absorption band could be attributed to the S1 \rightarrow Sn transition. The P-II band centered at 422 nm exhibits a starting absorption at the delay time of about 349 ps and its kinetic trace shows a continuous growth in the whole measured time range, implying that the concentration of this species increases in this time range. This feature suggests that this band should be induced by T1–Tn absorption. As for 3b, the P-I band absorption was centered at 545 nm and exhibits a continuous increase in intensity till the time delay of 159 ps. However, the P-II band absorption in the blue region was observed to be weak. This indicates that S1-T1 intersystem crossing is partially prohibited after the introduction of the alkyl chain into 5-phenyl-benzo[g]furo[2,3-b]quinoxaline.

As can be seen from the time-resolved fluorescence spectra shown in Fig. S1 (see the ESI[†]), compounds **3b** and **3c** with alkyl chains show slightly slower fluorescence decays in comparison to that of the protype compound **3a**. Moreover, **3a** exhibits a three exponential decay with a time constant $\tau = 0.78$ ns, 3.1 ns and 10.2 ns, respectively, while **3b** and **3c** show a single exponential decay with $\tau = 2.8$ ns. The results from the fluorescence decay measurement imply that photoluminescence of the three compounds is all from prompt fluorescence. From the time-resolved measurements, we can make a conclusion that the introduction of the alkyl chain into 5-phenyl-benzo[g]furo[2,3-b]-quinoxaline, although having little effect on the steady state photophysical properties, exerts a significant influence on its excited state dynamic processes.

2c. Electrochemical and thermal properties

The cyclic voltammetry (CV) results shown in Fig. 4a indicate that the three compounds **3a–3c** show one quasi-reversible reduction wave at -1.98, -2.28, and -2.30 V (*vs.* Fc/Fc⁺), respectively. Obviously, introducing the alkyl chain to the 2-phenylbenzo-[g]furo[2,3-*b*]quinoxaline skeleton made the resulting compounds harder to reduce, which could be attributed to the electron donating property of the alkyl chain. The respective onset reduction potentials (*vs.* Fc/Fc⁺) were calculated to be -1.79, -2.14, and -2.19 V, respectively. Based on these onset potentials, the LUMO levels were estimated to be -3.01 eV for **3a**, -2.66 eV for **3b**, and -2.61 eV for **3c**. Combining the LUMO data with the optical band gap obtained from absorption spectra in recorded CH₂Cl₂ solution, the HOMO



Fig. 4 (a) CV curves and (b) TGA curves of 3a-3c.

levels were determined to be -5.57 eV for 3a, -5.22 eV for 3b, and -5.18 eV for 3c, respectively. The HOMO energies were further estimated *via* ultraviolet photoelectron spectroscopy (see Fig. S2 in the ESI[†]).¹⁹ The ionization potential (IP) of 3a is -5.58 eV, matching well with the CV results, while the IP values of 3b and 3c were determined to be -5.47 eV and -5.51 eV, slightly lower than the corresponding CV results, respectively.

The thermal gravimetric analysis (TGA) result given in Fig. 4b shows that the decomposition temperatures of compounds **3a–3c** with a 5% loss are higher that 390 °C, which is higher than that of rubrene.^{10a} This result suggests that the three compounds exhibit favourable thermochemical stability. The DSC analysis (see Fig. S5 in the ESI†) indicated that **3a** only shows a melting temperature ($T_{\rm m}$) of 321 °C while compounds **3b** and **3c** with alky chains show both a glass transition temperature (132 and 127 °C) and $T_{\rm m}$ (184 and 155 °C). This indicates that the prototype compound **3a** is good for forming morphologically stable films while substitution modification of 2-phenylbenzo[*g*]furo[2,3-*b*]quinoxaline with alky chains could not contribute to a better morphological stability of the resulting materials.

2d. Morphological characterization

In order to elucidate the effect of the introduced alkyl chain on the semiconducting properties, X-ray diffraction (XRD) and atomic force microscopy (AFM) were used to investigate the morphology of the thin film samples deposited on an octadecyltrichlorosilane (OTS)/SiO₂/Si substrate. All the thin films were deposited on the substrate at room temperature. The three samples show one sharp peak in the XRD pattern, as shown in Fig. 5d, which revealed that the three compounds have excellent oriented-growth properties. The sharp peak for **3a** at $2\theta = 6.25^{\circ}$ can be assigned to the (001) reflection and thus a *d*-spacing of 14.14 Å could be calculated using Bragg's equation. This *d*-spacing distance is close to the



Fig. 5 AFM images of (a) 3a, (b) 3b and (c) 3c and (d) XRD patterns of thin films deposited on OTS-modified SiO₂/Si substrates.

calculated molecule length of **3a** (15.0 Å) using DFT theory. Therefore, we conclude that the **3a** molecule is present on the substrate face with an edge-on orientation. As for the thin films of compounds **3b** and **3c**, the sharp peaks appear at $2\theta = 3.75^{\circ}$ and 3.25° , respectively, and the calculated *d*-spacing distance (23.53 Å for **3b** and 27.13 Å for **3c**) is also comparable to the molecule lengths calculated by DFT theory (24.8 Å and 29.6 Å for **3b** and **3c**, respectively). For the same reason above, molecules **3b** and **3c** should also have an edge-on orientation to the substrate surface. In addition, the thin film of **3c** shows an additional peak at $2\theta = 6.25^{\circ}$ as compared with those of **3a** and **3b**, which may reveal the formation of a new phase.

The AFM images shown in Fig. 5a–c demonstrate that the thin films of **3a–3c** have different morphologies. The thin films of **3a** exhibit profoundly bigger grains than those of **3b** and **3c** in the AFM images, revealing that the introduction of the alkyl chain into the 5-phenylbenzo[g]furo[2,3-b]quinoxaline skeleton influences the thin film growth significantly. A series of experiments proved that a big grain size makes a beneficial contribution to higher mobility.^{3b} Thus, compound **3a** should show better transistor performance as a room-temperature deposited thin film. Based on the results of XRD and AFM, we can draw a conclusion that the introduction of the alkyl chain into 5-phenylbenzo[g]furo[2,3-b]-quinoxaline does not change the molecule orientation on the substrate surface, but it has an effect on the growth of grain size.

2e. OTFT properties

The bottom gate/top contact OTFTs with thin films deposited on the OTS modified SiO_2/Si substrate at room temperature were fabricated to estimate the semiconductor properties of **3a–3c**. Both **3a** and **3b** show p-type semiconducting properties supported by the output characteristics shown in Fig. 6a and b, in which the current increases with increasing negative gate voltage. Unexpectedly, no semiconducting behavior was observed for



Fig. 6 (a) Transfer and (b) output curves of **3a**-based thin film field-effect transistors; (c) transfer and (d) output curves of **3a**-based single crystal transistors.

the **3c**-based OTFTs whether the thin film was deposited on the SiO₂/Si substrate or the OTS/SiO₂/Si substrate. On the whole, the performances of the OTFTs with **3a** and **3b** thin films deposited on the OTS/SiO₂/Si substrate are significantly better than that on the bare SiO₂/Si substrate (see Table S2 in the ESI†). **3a** exhibits the best semiconductor performances among the three compounds. From the output and transfer curves of the OTFTs shown in Fig. 6a and b, the average hole mobility of the **3a**-based thin film transistors is 5.7×10^{-3} cm² V⁻¹ s⁻¹ with an $I_{\text{on/off}}$ ratio of 1.4×10^5 . But, the mobility of the **3b**-based thin film transistors is only 1.1×10^{-4} cm² V⁻¹ s⁻¹ and the $I_{\text{on/off}}$ ratio is 1.4×10^3 (see Fig. S3 in the ESI†).

Furthermore, the single-crystal transistors of **3a** with the bottom-gate/top-contact structure were fabricated by using the "gold stripe mask".²⁰ From their transfer and output characteristics depicted in Fig. 6c and d, the average hole mobility was deduced to be 2.58×10^{-2} cm² V⁻¹ s⁻¹, an order of magnitude higher than that of the thin film transistors. All the devices exhibit a favorable stability in air. Better performance could be expected by optimizing the fabrication conditions to obtain better crystallinity and continuity of the film, such as sifting a suitable self-assembly monolayer of the substrate or tuning the deposition temperature.

3. Conclusions

We developed a novel linearly fused aromatic molecular skeleton, 2-phenylbenzo[g]furo[2,3-b]quinoxaline, as a promising highly emissive organic semiconductor in the solid state. As we know, polyacenes with the number of fused aromatic rings of more than four are prone to undergoing singlet fission, resulting in exciton quenching. 2-Phenylbenzo[g]furo[2,3-b]quinoxaline exhibits favorable aggregation induced emission enhancement behavior and a reasonable hole mobility of 2.58×10^{-2} cm² V⁻¹ s⁻¹ for singlecrystal transistors. The absolute PLQY of 2-phenylbenzo[g]furo-[2,3-b]quinoxaline reaches up to 22.1% for powders and reaches a maximum of 19.7% in 50% water in THF. The correlation between the molecular structure and intermolecular interactions as well as the packing motif with the emissive and semiconducting properties will be investigated in further studies. It is likely that our molecular design consideration including using furan and N-heteroacene as building units and fixing heteroatoms on the same side of linearly fused heteroacenes would aid us to achieve more optimized molecular materials with efficient solid PLQYs and charge mobility.

4. Experimental section

4a. Synthesis and characterization

General procedure for synthesizing 2a–2c. To a 50 mL 3-neck flask, naphthalene-2,3-diamine (0.79 g, 5.0 mmol), 5-phenylfuran-2,3-dione (0.90 g, 5.1 mmol) and acetate acid (50 mL) were added. The mixture was heated to 110 $^{\circ}$ C for 5–8 h under nitrogen. Then, the reaction was allowed to cool down to room temperature and poured into water. The solid was collected by filtration, and washed

with methanol and DCM. The crude product was further purified *via* chromatography, and eluted with ethyl acetate to obtain the expected product **2a** (1.18 g, 3.8 mmol).

2a: (yield: 76%), ¹H-NMR (400 MHz DMSO): δ (ppm) 13.596 (s, 1H), 12.211 (s, 1H), 8.004–8.044 (t, 3H), 7.832–7.855 (t, 2H), 7.607–7.643 (t, 1H), 7.543–7.584 (t, 3H), 7.411–7.431 (t, 2H), 6.920 (s, 1H); MS (EI): m/z = 314 (M⁺).

2b: (yield: 67%), ¹H-NMR (400 MHz DMSO): δ (ppm) 13.569 (s, 1H), 12.183 (s, 1H), 7.937–7.972 (t, 3H), 7.823–7.846 (t, 2H), 7.531 (s, 1H), 7.403–7.427 (t, 2H), 7.359–7.379 (d, *J* = 8 Hz, 2H), 6.897 (s, 1H) 2.638–2.676 (t, 2H), 1.587–1.621 (t, 2H), 1.250–1.298 (m, 10H), 0.841–0.875 (t, 3H); MS (EI): m/z = 426 (M⁺).

2c: (yield: 79%), ¹H-NMR (400 MHz DMSO): δ (ppm) 13.575 (s, 1H), 12.188 (s, 1H), 7.943–7.982 (t, 3H), 7.830–7.851 (t, 2H), 7.537 (s, 1H), 7.408–7.428 (t, 2H), 7.367–7.387 (d, *J* = 8 Hz, 2H), 6.904 (s, 1H) 2.665–2.681 (t, 2H), 1.611 (t, 2H), 1.241–1.297 (m, 18H), 0.838–0.870 (t, 3H); MS (EI): *m*/*z* = 482 (M⁺).

General procedure for synthesizing 3a–3c. To a 50 mL 3-neck flask, 2a (0.74 g, 2.36 mmol) was added, then about 15 g of polyphosphoric acid was added, and the mixture was heated to 140 $^{\circ}$ C and stirred for 3 h. After cooling to room temperature, the mixture was poured into ice-water and neutralized with NaHCO₃, filtered, and the precipitate was purified *via* chromatography, and eluted with dichloromethane:petroleum ether (1:1) to obtain the expected product of 3a (yield: 0.51 g, 73%).

2-Phenylbenzo[g]furo[2,3-*b*]quinoxaline (**3a**): (yield: 73%), ¹H-NMR (400 MHz DMSO): δ (ppm) 8.861 (s, 1H), 8.766 (s, 1H), 8.256–8.297 (t, 2H), 8.197–8.221 (d, 2H), 7.957 (s, 1H), 7.641–7.678 (m, 5H); ¹³C: 165.43, 154.67, 146.40, 139.42, 136.09, 133.19, 132.91, 131.68, 129.24, 128.35, 128.33, 128.01, 126.87, 126.49, 126.42, 126.27, 100.80, 40.48, 40.27, 40.06, 39.64, 29.70; HRMS (ES): *m*/*z* calc. for C₂₀H₁₂N₂O 296.0950, found 297.10245 [M⁺ + H].

2-(4-Octylphenyl)benzo[g]furo[2,3-*b*]quinoxaline (**3b**): (yield: 71%), ¹H-NMR (300 MHz CDCl₃): δ (ppm) 9.02 (s, 1H), 8.85 (s, 1H), 8.55–8.56 (d, *J* = 4.5 Hz, 1H), 8.31–8.35 (m, 2H), 8.17–8.19 (d, *J* = 4.8 Hz, 1H), 7.82–7.85 (m, 1H), 7.70–7.72 (m, 3H); ¹³C: 165.84, 154.75, 147.52, 146.61, 139.46, 136.10, 133.09, 132.89, 129.35, 128.32, 128.01, 126.75, 126.46, 126.37, 126.20, 125.79, 99.99, 36.09, 31.88, 31.20, 29.45, 29.30, 29.24, 22.67, 14.11; HRMS (ES): *m*/*z* calc. for C₂₈H₂₈N₂O, 408.2202, found 409.22813 (M⁺ + H).

2-(4-Dodecylphenyl)benzo[g]furo[2,3-*b*]quinoxaline (3c): (yield: 70%), ¹H-NMR (400 MHz CDCl₃): δ (ppm) 8.855 (s, 1H), 8.731 (s, 1H), 8.151–8.194 (m, 2H), 8.024–8.044 (d, J = 8 Hz, 2H), 7.621–7.646 (m, 2H), 7.385–7.434 (t, 3H), 2.722–2.761 (t, 2H), 1.663–1.717 (m, 4H), 1.284–1.301 (m, 16H), 0.882–0.916 (m, 3H); ¹³C: 155.02, 148.33, 133.19, 129.50, 128.32, 128.08, 126.83, 126.72, 99.40, 50.86, 40.09, 36.16, 31.92, 31.16, 29.67, 29.65, 29.57, 29.48, 29.36, 29.29, 22.70, 14.13; HRMS (ES): *m/z* calc. for C₃₂H₃₆N₂O 464.2828, found 465.29085 (M⁺ + H).

4b. General procedure and experimental details

Materials and instruments. Reagents were used without further purification. ¹H-NMR and ¹³C NMR spectra were recorded

on Bruker Avance 300 MHz spectrometers. HRMS experiments were carried out on a Thermo Scientific LTQ Orbitrap Discovery (Bremen, Germany). TGA-DTA measurements from room temperature to 500 °C were carried out on a Shimadzu DTG-60 instrument under a dry nitrogen flow with a heating rate of 10 °C min⁻¹. Cyclic voltammograms were recorded on a Princeton Applied Research model 273 A electrochemical workstation at a scan rate of 100 mV s⁻¹ using 0.1 M tetrabutylammonium perfluorinated phosphorate (TBAPF6) as a supporting electrolyte in dry CH2Cl2. Glassy carbon, Pt-sheet and Pt-wire were employed as the working electrode, counter electrode and reference electrode. During each measurement, the cell was purged with a nitrogen flow for some time and ferroceninium/ferrocene (Fc/Fc⁺) was used as the internal reference. UPS (KRATOS Axis Ultra DLD spectrometer) measurements were performed with a base pressure $> 2 \times 10^{-9}$ Torr and He I (h = 21.22 eV) as the excitation source. UV-visible spectra of solutions and powders were recorded on Hitchi 3010 spectrometers. An FLS 980 fluorescence spectrometer was used to measure steady state and transient fluorescence spectra. Fluorescence quantum yields (PLQYs) were measured by using the integrating sphere in combination with the FLS980 spectrofluorometer.

The fs-TA measurements were performed on a Helios pumpprobe system (Ultrafast Systems LLC) combined with an amplified femtosecond laser system (Coherent). An optical parametric amplifier (TOPAS-800 fs) provided a 365 nm pump pulse (~8 nJ per pulse at the sample), which was excited by a Ti: sapphire regenerative amplifier (Legend Elite-1K-HE; 800 nm), 35 fs, 7 mJ per pulse, 1 kHz) and seeded using a mode-locked Ti: sapphire laser system (Micra 5) and pumped using a Nd:YLF laser (Evolution 30).

Thin film X-Ray diffraction was performed in reflection mode at 40 kV and 200 mA with Cu K radiation using a 2 kW Rigaku D/max-2500 X-ray diffractometer. X-ray diffraction intensity data were collected at 113 K on a Rigaku Saturn 724 CCD diffractometer with graphite monochromated Mo K α radiation. AFM images were obtained by using a Digital Instruments Nanoscope III atomic force microscope in air. Thin films for AFM investigation were identical to those employed for the fabrication of organic filed-effect transistors. OFET characteristics were recorded by using a Keithley 4200 SCS and Micromanipulator 6150 probe station in a clean and shielded box at room temperature.

4c. Device fabrication and measurement

Thin film field-effect transistors of 3a–3c. For the fabrication of bottom-gate/bottom-contact OFETs, an n-type Si wafer with a SiO₂ layer of 300 nm and a capacitance of 11 nF cm⁻² was used as the gate and dielectric, respectively. Photolithography was employed to prepare the drain–source (D–S) gold contacts. Molecules of 3a–3c (about 50 nm in thickness) were deposited (0.1 Å s⁻¹) under vacuum onto the Si/SiO₂ substrate, or the Si/SiO₂ substrate modified by OTS at room temperature.

Single crystal field-effect transistor of 3a. The device fabrication of bottom-gate top-contact single-crystal field-effect transistors followed the following procedures. (1) The heavily doped, n-type Si wafer with a 300 nm-thick SiO₂ layer was used as the substrate. After piranha cleaning $(H_2SO_4:H_2O_2 = 7:3, volume ratio),$ the substrate was then successively cleaned with pure water, pure isopropanol and oxygen plasma (5 min, 100 W). (2) Surface modification of the Si/SiO2 wafer with OTS was then carried out by using the vapor deposition method in a vacuum chamber (0.1 Pa). The Si/SiO₂ wafer was first dried at 90 $^{\circ}$ C (1.5 h) to remove the moisture and then kept at 120 °C (2 h) to allow for the deposition of OTS. After cooling down to room temperature, the substrate was washed successively with n-hexane, trichloromethane and isopropanol for the following device fabrication. (3) Single crystals of 3a were in-situ grown on the OTS/SiO₂/Si substrate by physical vapor transport in a two zone horizontal furnace under 3 Pa, with 3a powder in the high temperature zone and the substrate in the low temperature zone for OFET fabrication. (4) The "organic ribbon mask" method was used to construct devices on an individual single crystal for charge transport investigation. Micrometre or sub-micrometre organic ribbon prepared in advance on other substrates was peeled off and put directly on a pre-deposited 3a crystal using a micromanipulator 6150 probe station under a high-resolution microscope (magnification at X40-200). The substrate was transferred to a vacuum chamber and 40 nm of gold was deposited on the masked single crystals. The field-effect devices were prepared by peeling off the ribbons. (5) The field-effect transistor characteristics were measured at room temperature in air on a Keithley 4200 SCS and micromanipulator 6150 probe station and the mobility was extracted from the saturation region by using the equation of IDS = $(W/2L)C_i\mu(V_G - V_T)^2$.

Author contribution

Gang Wang, Yixiang Li, Jingjing Zhang and Dongdong Wang contributed to the synthesis of new materials and photophysical characterization. Li Jie, Zhen Yonggang, Hu Wenping and Tang Qingxing contributed to the device characterization. Wu Zhaoxin, Ma Hong, Alex Jen and Wang Dongdong contributed to the molecular design and manuscript preparation. Yong Wu performed the theoretical calculations.

Conflicts of interest

There are no conflicts to declare.

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