A scalable and convenient strategy is described to synthesize extended conjugation quinoxaline derivatives from phenylene-ethynylene arrays. By tuning the solvent, the compounds display bright emission solvatochromism. Furthermore, the fabricated FET devices possess good performance characteristics, with mobilities of 0.47 cm² V⁻¹ s⁻¹ and 0.99 cm² V⁻¹ s⁻¹. The mobilities are higher than those of corresponding to the alkyl substituted compounds, which can be proven by grazing incidence X-ray diffraction (GIXRD) measurement.

Hetero- and polycyclic aromatic hydrocarbons (hetero-PAHs) have attracted increasing attention for their design, synthesis and application because of some fascinating features, such as high stability, low energy absorption, and high charge carrier mobility. Among the large N-substituted heterocycles that are pervasive in natural products, biologically active agents and part structures in functional π-systems, quinoxalines are extraordinarily attractive. Several derivatives have been proven to possess in vitro antiparasitic and anti-tumor activities, and some have been used as 5-HT3 receptors or kinase inhibitors. In addition, quinoxalines have also been applied as building blocks for the development of semiconducting materials, fluorescent probes, sensors, anion receptors and cavatands. In general, the reaction features condensation of 1,2-diamines with diketones to afford quinoxaline derivatives. Recently, a one-pot strategy has been proposed to construct quinoxaline oligomers using expensive metal catalysts, followed by tedious isolation procedures.

Due to this consideration, a series of conjugation extended quinoxalines are prepared using a simple catalyst and facile isolation. Dicarbonyl derivatives, as intermediate products, have been obtained without much effort, and are useful building blocks capable of undergoing various chemical transformations. Different π-conjugated phenylene-ethynylene arrays were used as starting compounds to control the sequence of the conjugation chain of final products. The insertion of electron-withdrawing quinoxalines on the phenylene-ethynylene backbone influences the electronic structures and various properties of the resulting compounds. Alkyl chains (n-butyl) are introduced to the compounds to improve solubility.

The oxidation of alkynes was catalyzed efficiently by PdCl₂ to afford intermediate products 5–8, in which DMSO acted as a powerful oxidant (Scheme 1). The condensation reaction of compounds 5–8 and 1,2-phenylenediamine successfully afforded quinoxaline derivatives 9–12 in good yields, after plain filtration of 5–8. Bruenet products were avoided and white solids finally precipitated after these two separate steps. In our experimentation, the stepwise process was the key to obtain...
pure products in high yields, which was verified by $^1$H NMR and $^{13}$C NMR (Fig. S1–S40†). With the increase in the $\pi$-conjugated skeleton, 11–12 are poorly soluble in acetic acid, leading to their nearly complete precipitation from the reaction mixture. A needle-like single crystal of 10b was obtained by recrystallization from acetic acid. The X-ray analysis was conducted to establish the structure shown in Fig. 1 and Table S1.

The ultraviolet/visible (UV/vis) absorption and photoluminescence (PL) spectra of 9–12 in chloroform are shown in Fig. S41 and S42,† and the data are compared in Table 1. The extended structural unit affects the position of the absorption and emission bands across the series from 9 to 12, although the red-shift is not prominent. However, the electron-donating effect of the $n$-butyl substituent results in a red-shift of the longer wavelength absorption band to ca. 390 nm, which changes the electron cloud density of the adjacent benzene ring. In chloroform, compound 12b emits deep blue photoluminescence with an emission maximum at 418 nm. However, the emission changes to bright green in acetone solution. Depending on the identity of the solvent, its polarity results in quite positive and significant changes to the emission wavelength, ranging from 432 to 518 nm (Fig. 2a). This pronounced positive emission solvatochromism is observable with naked eyes, where the color changes from blue (toluene) to yellow-green (DMSO) (Fig. 2a). More polarizable solvent served to stabilize the excited state more than the ground state, which lessens the energy gap.†7 We also determined the photophysical properties of 12a in the same solvents and observed a similar bathochromic trend, exhibiting PL emission maxima in the range from 480 to 525 nm (Fig. 2b).

The introduction of an electron-donating or electron-accepting group directly affects the HOMO and LUMO levels of the compounds. The cyclic voltammetry curves of quinoxaline derivatives 9–12 show no reversible peaks arising from the oxidation potential, which is ascribed to the electron-deficient pyrazine ring containing two sp$^2$-type centers (Fig. S43†).†8 In the anodic scan, the onset of oxidation for 9a–12a occurs at 1.06, 0.88, 0.75 and 0.70 V, which corresponds to HOMO values of $-5.81$, $-5.63$, $-5.50$ and $-5.45$ eV, respectively (Table 2). The oxidation potential values of alkylated oligomers follow the order 9b > 10b > 11b > 12b; this is the same trend that is evident for compounds 9a–12a. The extended conjugation length slightly raises the HOMO level and consequently reduces the band gap of the oligomers. The energy band gaps of 9a–12a are calculated to be 3.28, 3.18, 3.15 and 3.12 eV, as determined from the onset wavelength of their UV absorptions. The HOMO–LUMO energy gaps show good correlation with their UV data and the molecular extended conjugation chain.

The transfer integral and reorganization energy, which are believed to be important for the mobility of semiconductors, are both based on the arrangement of the organic molecules.†9 To

### Table 1 Photophysical properties of compounds 9a–12a and 9b–12b

<table>
<thead>
<tr>
<th>Sample</th>
<th>UV (λ$\text{max}$/nm)</th>
<th>PL (λ$\text{max}$/nm)</th>
<th>Φ $\text{F}_s$ (a,b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>345</td>
<td>413</td>
<td>5.23</td>
</tr>
<tr>
<td>10a</td>
<td>358</td>
<td>416</td>
<td>10.35</td>
</tr>
<tr>
<td>11a</td>
<td>359</td>
<td>421</td>
<td>31.32</td>
</tr>
<tr>
<td>12a</td>
<td>359</td>
<td>425</td>
<td>54.37</td>
</tr>
<tr>
<td>9b</td>
<td>390</td>
<td>416</td>
<td>5.32</td>
</tr>
<tr>
<td>10b</td>
<td>394</td>
<td>417</td>
<td>11.24</td>
</tr>
<tr>
<td>11b</td>
<td>395</td>
<td>417</td>
<td>35.11</td>
</tr>
<tr>
<td>12b</td>
<td>396</td>
<td>418</td>
<td>62.33</td>
</tr>
</tbody>
</table>

(a) Absorption maximum in dilute CHCl$_3$ solutions. (b) Quantum yield estimated with quinine sulfate (Φ $\text{F}_s$ = 54% in 0.1 M H$_2$SO$_4$).
Table 2  Electrochemical properties of compounds 9a–12b

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{onset}}^{\text{ox}}$ (V)</th>
<th>HOMO (eV)</th>
<th>$\lambda_{\text{onset}}$ (nm)</th>
<th>$\Delta E_g$ (eV)</th>
<th>LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>1.06</td>
<td>$-5.81$</td>
<td>378</td>
<td>3.28</td>
<td>$-2.53$</td>
</tr>
<tr>
<td>10a</td>
<td>0.88</td>
<td>$-5.63$</td>
<td>389</td>
<td>3.18</td>
<td>$-2.45$</td>
</tr>
<tr>
<td>11a</td>
<td>0.75</td>
<td>$-5.50$</td>
<td>394</td>
<td>3.15</td>
<td>$-2.35$</td>
</tr>
<tr>
<td>12a</td>
<td>0.70</td>
<td>$-5.45$</td>
<td>397</td>
<td>3.12</td>
<td>$-2.33$</td>
</tr>
<tr>
<td>9b</td>
<td>0.96</td>
<td>$-5.71$</td>
<td>390</td>
<td>3.18</td>
<td>$-2.53$</td>
</tr>
<tr>
<td>10b</td>
<td>0.86</td>
<td>$-5.61$</td>
<td>395</td>
<td>3.14</td>
<td>$-2.47$</td>
</tr>
<tr>
<td>11b</td>
<td>0.73</td>
<td>$-5.48$</td>
<td>396</td>
<td>3.13</td>
<td>$-2.35$</td>
</tr>
<tr>
<td>12b</td>
<td>0.69</td>
<td>$-5.44$</td>
<td>398</td>
<td>3.12</td>
<td>$-2.32$</td>
</tr>
</tbody>
</table>

* Abbreviations: $E_{\text{onset}}^{\text{ox}}$ is the onset potential for oxidation. HOMO is calculated by the equation: HOMO = $-e(E_{\text{onset}}^{\text{ox}} - 0.0468 V) - 4.8$ eV. $\lambda_{\text{onset}}$ is the onset wavelength of UV absorptions. LUMO = $\Delta E_g + \text{HOMO}$. 

Further inspection and comparison of the molecular packing characteristics of quinoxaline derivatives with the extended skeleton, two-dimensional grazing incidence X-ray diffraction (2D-GIXRD) measurements were performed. As for oligomer 12a, the clear (100) reflection arc appears along the $q_z$ direction with a value of 11.2 nm$^{-1}$ (Fig. 3a). Furthermore, a clear arch shape of the (010) diffraction peak in the in-plane direction appears at $q_{xy} = 18.01$ nm$^{-1}$, which corresponds to the π-π stacking distance of 3.49 Å. Evidently, 12a tends to pack more orderly and tightly than 12b in neat films, which may be due to the steric hindrance caused by the alkyl chains. The prominent (010) arch of compound 12b appears at $q_{xy} = 17.50$ nm$^{-1}$, with π-π distance of 3.59 Å (Fig. 3b). Compared with the variation in π-π stacking, the alkyl substituent is of larger influence for the spacing in the out-of-plane direction. The intense reflections of the (100) plane along the $q_z$ (out-of-plane) axis and a relatively weak (010) plane along the $q_{xy}$ (in-plane) axis of 12b films can be observed from Fig. 3b, which implies that 12b molecules would prefer to have an edge-on structure. The ordered edge-on structure of organic molecules prefers to be formed in high performance FETs, which allows the molecules to arrange along the direction of the conducting channel and then get an efficient charge transport. In addition, the decreased length of the conjugated chain makes some differences. Compared to 12a, the out-of-plane spacing of 11a increased to 5.66 Å and the π-π stacking distance also rose to 3.50 Å (Fig. S44†).

The higher HOMO energy level suggests that 12 might have great potential for use in field-effect transistors (FETs) as p-type materials. Furthermore, N-heteroatoms provide a new method of tuning the intrinsic molecular electronic properties and improving stability, which have been extensively studied areas for organic thin film transistors. Quinoxaline derivatives 11a–12a and 11b–12b have high thermal stabilities, which are beneficial for the processing of electrical devices (Fig. S45†). We evaluated the charge transport properties of the oligomers 11a–12a and 11b–12b by fabricating field-effect transistors in the “top-contact top-gate” geometry. To this end, FETs using the quinoxaline derivatives were fabricated using ion gels to efficiently diminish the heat generated at work and to endow low voltage operation. Moreover, top-gated quinoxaline derivative transistors prepared using ion gel gate dielectrics have been rarely reported. The representative transfer curve ($I_D - V_G$) of the FET with 11a is displayed in Fig. 4a and that of the 12a is shown in Fig. 4c. The best results of 11a and 11b devices exhibit mobilities up to 0.47 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.44 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, with on/off ratios up to 10$^3$ (Fig. S46†). Significant increases of the mobilities are also observed in the 12a, 12b based devices of 0.99 cm$^2$ V$^{-1}$ s$^{-1}$ and 0.88 cm$^2$ V$^{-1}$ s$^{-1}$, respectively, as evaluated from the saturation regime (Fig. S47†). In addition, the output characteristics ($I_D - V_D$) of the aluminum-gated quinoxaline derivative based FETs at five different gate voltages ($V_G$) are shown in Fig. 4b and d, affirming the clear p-channel characteristics. The structure–property relationship has been verified by a range of analyses, particularly using 2D-GIXRD. The substantial structural change has an enormous influence on the packing of the neighboring molecules, which in turn affects the specific properties. The extended conjugation chain and the closer structures did have a great

Fig. 3  The 2D-GIXRD pattern of (a) 12a and (b) 12b.

Fig. 4  (a) Transfer and (b) output characteristics of the 11a devices ($W = L = 1000$ μm) at a drain source voltage ($V_{DS}$) of 2.5 V. (c) Transfer and (d) output characteristics of the 12a based FETs.
influence on the conductive properties according to the above comparisons. The mobility of 12 is among the best results ever reported for N-heteroatoms.\textsuperscript{25}

**Conclusions**

In summary, a series of extended conjugation quinoxaline oligomers 9–12 have been successfully synthesized by a convenient and efficient route with a simple isolation procedure. The compounds 12a and 12b display positive emission solvatochromism, as revealed by detailed optical studies. The performance of 11a and 12a based FET devices is comparable, showing mobilities of 0.47 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for 11a and 0.99 cm\textsuperscript{2} V\textsuperscript{-1} s\textsuperscript{-1} for 12a. Furthermore, the FETs fabricated with 11b and 12b are also measured, and mobilities are lower than those of 11a and 12a. The employment of 2D-GIXRD provides a direct explanation for the difference in FET performance between 12a and 12b, in which the alkyl chain weakens the molecular packing.

**Acknowledgements**

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**Notes and references**


23. (a) H. Okamoto, R. Eguchi, S. Hamao, H. Goto, K. Gotoh, Y. Sakai, M. Izumi, Y. Takaguchi, S. Gohda and...
