Synthesis of a soluble poly(fluorenone)†

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The synthesis and characterisation of a soluble poly(fluorenone) is presented, a polymer with high electron affinity with potential for use in plastic electronic devices as an n-type material.

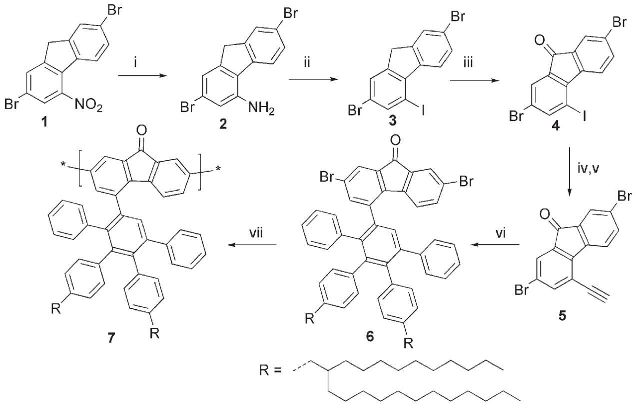
The field of polymer optoelectronics has witnessed a great deal of progress since the discovery of the conducting properties of polyacetylene in 1977.[1] Derivatives such as poly(9,9-dialkylfluorene)s have received considerable attention as candidates for the active material in optoelectronic devices such as organic light-emitting diodes (OLEDs), due to their good chemical stability and high luminescence quantum efficiency.[2,3] The majority of emitting polymers currently in use are largely hole-transporting in character, *i.e.* p-type materials. In comparison, there are relatively few reports on electron-deficient conjugated polymers, in other words conjugated polymers with low lying conduction bands and high electron affinity (EA).[4,5] Polymers of this nature would not only be useful in OLEDs as electron transport materials (ETM) for increased electron injection from the cathode and as hole blockers, but could also serve as an n-type material for use in photovoltaic devices.

The properties that govern the effectiveness of a polymer for use as an ETM include its EA, ionization potential (IP), electron mobility, and electrochemical and thermal stabilities. The most widely studied organic structural types among ETMs are those containing oxadiazoles,[6–10] various N-containing heteroaromatics,[11–15] and perfluorinated aromatic materials.[16,17] One promising class of polymers that has received less attention, mainly due to the inability to synthesize readily processable materials, are aromatic polyketones. Fluorenone has been incorporated in various copolymers in the past.[18,19] The homopolymer 2,7-poly(9-fluorenone) was first reported as an unprocessable film deposited on an electrode after electrochemical polymerization.[20] The preparation of 2,7-poly(9-fluorenone) films from a spin cast soluble precursor (polyfluorene ketal) resulted in a promising ETM, however it involved a polymer analogous deprotection to give the insoluble ketone.[21,22] Fluorenone is known to act as a charge-trapping, low energy defect in polyfluorene based materials; however, this is not the issue for the fluorenone homopolymer.[23] Herein, we describe the synthesis of the first highly soluble 2,7-poly(9-fluorenone) **7**, which is easily processable and has good film forming properties.

As polyfluorene is typically solubilized with substituents at the 9 position, an alternative substitution is required for 9-fluorenone. Our approach is to attach a bulky alkylated tetra-phenyl benzene unit to the 4-position to increase solubility and processability. The attached alkyl substituents have been previously shown to enhance the solubility of strongly aggregating materials. The synthesis of a soluble 2,7-poly(9-fluorenone), which can be performed on a large scale, is shown in Scheme 1.

Commercially available 2,7-dibromo-fluorene was nitrated according to literature procedures to generate **1**.[24] The Clemmensen reduction of **1** followed by a Sandmeyer reaction gave the 2,7-dibromo-4-iodo-fluorene **3**. **3**, together with tetrabutylammonium hydroxide as a phase transfer catalyst, was dissolved in pyridine and oxidized with oxygen gas to the tri-halo fluorenone. A Hagihara–Sonogashira cross coupling reaction allowed the coupling of 2,7-dibromo-4-iodo-fluorenone with trimethylsilyl acetylene, which was deprotected to yield **5**. Diels–Alder reaction of **5** with a dialkyl substituted tetraphenyl cyclopentadienone gave the tetraphenyl benzene dendrimer substituted fluorenone monomer, **6**. 2,7-Poly(9-fluorenone) (**7**) was obtained by Yamamoto polymerization of **6** according to the standard procedure.

7 was soluble in common organic solvents such as toluene and THF. The gel permeation chromatography (GPC) of **7** showed a monomodal distribution with a number-average molecular weight (M_n) of 2.6×10^4 g mol^{-1} (poly-*para*-phenylene standard). This corresponds to a number average degree of polymerization of approximately 20 repeat units. Thermogravimetric analysis (TGA) indicated that **7** has good thermal stability up to 400 °C. The differential scanning calorimetry (DSC) analysis demonstrated that **7** has an amorphous structure with no phase transition between



Scheme 1 Synthesis of a dendronised 2,7-poly(9-fluorenone). i) HCl, Sn, EtOH reflux; ii) H_2SO_4, $NaNO_2$, 0 °C, then KI, 100 °C; iii) $(C_4H_9)_4NOH$, O_2, pyridine, r.t.; iv) TMS-acetylene, CuI, PPh_3, $Pd(PPh_3)_4$, r.t.; v) K_2CO_3, THF, water, r.t.; vi) substituted tetraphenyl cyclopentadienone, *o*-xylene, 150 °C; vii) Ni(COD)$_2$, COD, bipy, toluene, DMF, 80 °C.

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−100 °C and 350 °C, due to the bulky tetraphenyl benzene substituents.

The UV/vis absorption and fluorescence spectra of **7** in a dilute THF solution and a thin film drop cast from a toluene solution are shown in Fig. 1. The polymer showed two maxima in the absorption spectrum at 367 nm and 456 nm in solution. The higher energy maximum at 367 nm corresponds to the π–π* transition of the polyphenylene backbone, while the weaker absorption at lower energies corresponds to the symmetry forbidden n–π* transition of the carbonyl function.[21] The hypsochromic shift of the π–π* transition suggested that the sterically hindered polymer is highly twisted. Although this negatively effects the conjugation of the polymer, the interchain charge transport would not be adversely affected. The thin film absorption spectrum showed a typical bathochromic shift relative to the solution absorption spectrum. The fluorescence emission maxima of **7** in solution and thin film were 524 nm and 554 nm, respectively (excitation wavelengths 365 nm and 360 nm, respectively). The emission spectrum of **7** in solution showed a shoulder at 550 nm, which we attribute to excimer formation as the shoulder emission is at the same position as the thin film emission maximum. This is supported by concentration dependent photoluminescence spectroscopy, which demonstrated the relative increase of the intensity of the emission at 550 nm with increasing concentration (see ESI†). There is no observed emission from the polyphenylene backbone, indicating complete energy transfer to the carbonyl chromophore. The spectroscopic properties of **7** were comparable to the previously published spectra of fluorenone containing polyfluorene materials.

In order for **7** to be considered an ETM, it must show a reversible reduction.[5] The differential pulse voltammogram of a film of **7** is presented in Fig. 2. The differential pulse voltammogram exhibited a reversible reduction with a reduction potential of −1.29 V *vs.* AgQRE for **7**. An estimation of the EA is possible from the reduction potential by calibration with ferrocene/ferrocenium standard, which has a vacuum energy level of −4.8 eV. This resulted in an EA of −3.0 eV for **7**. The EA of polyfluorenone prepared from the ketal precursor was found to be −3.3 eV.[21] Polymer **7** may not be as easy to reduce compared to the insoluble polyfluorenone due to the tetraphenylbenzene side chain, which shields the ketone moiety, making it less susceptible for reduction. In comparison with a prevalent ETM, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), with a EA of −2.4 eV, the EA of −3.0 eV of **7** results in a reduced energy barrier to electron injection from the cathode, *e.g.* Mg (Φ = −3.7 eV).[25] Other electron deficient polymers that have been used in the past as the ETM lack redox stability. Cyano substituted PPV, CN-PPV, has been successfully used as the ETM in an OLED, but shows an irreversible reduction.[26,27]

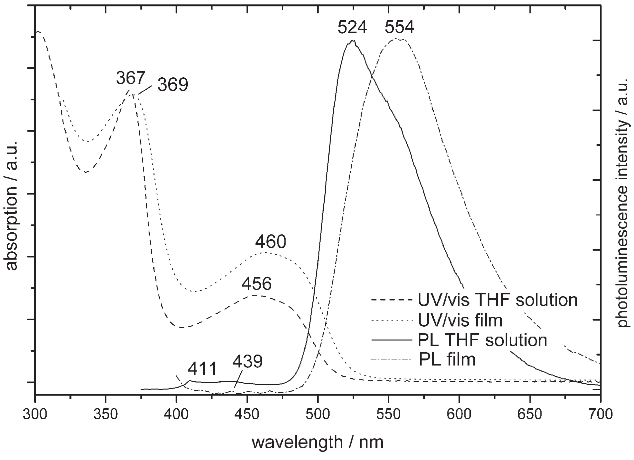

Fig. 1 UV/vis and photoluminescence spectra of **7** from THF solution and film.

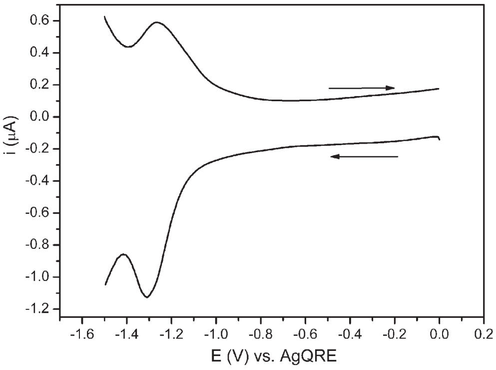

Fig. 2 Differential pulse voltammogram (reduction) of **7** *vs.* AgQRE (film on gold, 0.1 M $TBAClO_4$ in acetonitrile).

In summary, we present the synthesis of a soluble polyfluorenone. By attaching a bulky tetraphenylenebenzene at the 4-position of fluorenone, a soluble polymer can be prepared with good film forming properties. This negates the need for any undesirable protection and deprotection steps in the synthesis. The differential pulse voltammogram of the polymer demonstrated that the reduction of the carbonyl group is fully reversible. Investigations into the charge carrier mobility of **7**, and its incorporation into photovoltaic devices, are currently in progress.

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