Flow Photochemical Synthesis of Thiophene-fused Organic Semiconductors

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In the past decades, many polycyclic heteroaromatic compounds have been developed as semiconductors for organic field effect transistors (OFETs). To construct polycyclic aromatic skeletons, photoinduced electron transfer (PET)-assisted tandem cyclization-dehydrogenation

reaction is a typical strategy (Scheme 1). Actually, more efficient synthesis of these compounds can be achieved by utilizing photochemical flow



Scheme 1. Tandem 6π -cyclization–dehydrogenetion reactions to provide polycyclic aromatic compounds.

reactors. In this work, we synthesized alkyl-substituted tetrathienonaphthalenes (TTN) and trithia[5]helicene derivatives (Scheme 1)^{1,2} and fabricated OFET utilizing solution process. Also, we carried out theoretical prediction of hole mobility of C_n -TTN was based on

<u>a</u>morphous <u>solid</u> <u>simulation-statistics</u> (ASSiST) method.³

Theoretical Simulation. Amorphous solid structure of 480 molecules of C_n -TTN was obtained by annealing (1000 K, 2 ns)– cooling (300 K, 1 ns) process in molecular dynamics simulation under periodic boundary condition (Fig. 1). Hole transfer rate constant (*W*) was obtained by using transfer integral (*t*) of a given focused molecules and the neighboring molecules and Marcus equation (eq. 1), where *h* is Planck constant, λ_{RE} is reorganization energy, k_B is the Boltzmann constant, and *T*



Fig. 1. Method for preparation of the amophous solid structure of C_6 -TTN: (a) initial ordered configuration, (b) random configuration, and (c) created structure.

$$W = \frac{2\pi t^2}{h} \left(\frac{\pi}{\lambda_{\rm RE} k_{\rm B} T}\right)^{1/2} \exp\left[-\frac{\lambda_{\rm RE}}{4k_{\rm B} T}\right] \quad (1) \qquad \mu_{\rm am} = \prod_{N} \left(\frac{1}{6} \frac{e}{k_{\rm B} T} \frac{\sum_{i} r_i^2 W_i^2}{\sum_{j} W_j}\right)^{1/N} \quad (2)$$

is the temperature. Furthermore, hole mobility of the amorphous structure (μ_{am}) is estimated as a geometric mean using the modified Stokes–Einstein equation (eq. 2),³ where N is the number of "molecular flocks", e is the elementary charge, and r is the distance between molecular centroids. Using this approach, we found that μ_{am} values are calculated to be 2.1 × 10⁻², 9.3 × 10⁻³, and 1.8 × 10⁻³ cm² V⁻¹ s⁻¹ for C₆-, C₈-, and C₁₀-TTNs, respectively (Table 2). These values indicate that too long alkyl chains decrease μ_{am} in the amorphous solid and/or crystal boundary, due to reduction of t.

Photochemical Synthesis. Photoirradiation [$\lambda_{EX} = 350$ nm, 3–6 h] of a CH₂Cl₂ solution containing C_n-TTE and *p*-chloranil (*p*-CA, 2 eq) in a batch reactor led to a formation of C_n-TTN in 24–58% yield (Table 1). Use of a microflow reactor (1 × 0.5 × 915 mm) improved these reaction yields, up to 73% in an extremely short residence time. These results were explained by homogenous photoirradiation and prevention of overreaction by discharge from the reactor, originated from the effects of flow reactor.

OFET Characteristics. Thin polycrystalline films (~100 nm) of C_n-TTN were obtained by using spin-coating of the toluene solution (1 wt%) on glass substrate. The films were conducted to fabrication of top-gate bottom-contact OFET with moderate p-type characteristics with $\mu_{OFET} \sim 10^{-2}$ cm² V⁻¹s⁻¹ (Table 2). In the presentation, we also discuss interesting relationship between alkyl chain length and μ_{OFET} , and understanding of relationship between μ_{am} and μ_{OFET} .



^aResidence time

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