Supplementary Information

Explicit analysis of functional-group orientation in amorphous organic semiconductor films by using deuterated materials

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Fig. S1 AFM image of a 100-nm-thick BPBPA-D0 film deposited on a Si(100) substrate. The RMS value of the surface roughness is 0.27 nm.

Fig. S2 (a) Out-of-plane and (b) in-plane XRD patterns of a 100-nm-thick BPBPA-D0 film deposited on a Si(100) substrate.
Fig. S3 Anisotropic refractive indices and extinction coefficients of 100-nm-thick as-deposited films of (a) BPBPA-D0, (b) D1, and (c) D2 determined by VASE.

Fig. S4 Anisotropic refractive indices and extinction coefficients of 100-nm-thick annealed films of (a) BPBPA-D0, (b) D1, and (c) D2 determined by VASE.
Fig. S5 Steric structures and transition dipole moment vectors for low-energy electronic transitions of the 24 conformers of BPBPA molecules. The differences in the steric energy are also shown as $\Delta E$. (Continued on next page)
Fig. S5
(Continued from the previous page)
Conformer 17
(ΔE = 0.026 eV)

Conformer 18
(ΔE = 0.026 eV)

Conformer 19
(ΔE = 0.026 eV)

Conformer 20
(ΔE = 0.027 eV)

S₁  S₂  S₃  S₁  S₂  S₃  S₁  S₂  S₃  S₁  S₂  S₃

(10.1  0  0  0.2  0.1  0.5  0.1  0.1  0.5  0.2  0.1  0.5)

(0.1  7.5  8.0  1.9  0  0.5  7.5  8.0  0.5  7.5  8.0  0.5)

(0.1  0.6  0.6  0.6  0.6  0.6  0.6  0.6)

(debye) (debye) (debye)

Conformer 21
(ΔE = 0.028 eV)

Conformer 22
(ΔE = 0.033 eV)

Conformer 23
(ΔE = 0.034 eV)

Conformer 24
(ΔE = 0.040 eV)

S₁  S₂  S₃  S₁  S₂  S₃  S₁  S₂  S₃  S₁  S₂  S₃

(10.3  0  0  10.1  0  0  10.2  0  0  10.1  0  0)

(0  7.9  7.4 -0.1  4.6  0  0  2.5  0  0  2.5  0)

(0  0  0  0  0  0  0  0  0  0  0  0)

(debye) (debye) (debye) (debye)

Fig. S5
(Continued from the previous page)
Fig. S6 Simulated IR absorption spectra of (a) BPBPA-D0, (b) D1, and (c) D2 molecules obtained by DFT B3LYP/6-31G(d) calculations.
Fig. S7 Dependence of IR absorption spectra of 100-nm-thick as-deposited and annealed (a) BPBPA-D0, (b) D1, and (c) D2 films on the deposition rate in the spectral range of 1100–1700 cm$^{-1}$. 
**Fig. S8** $J-V$ characteristics for negative voltage side of three hole-only devices A, B, and C, where BPBPA-D0 is deposited at three different deposition rates of 0.2, 2, and 20 Å s$^{-1}$, respectively; Device A, B, and C: glass/ITO (75 nm)/HAT-CN (5 nm)/BPBPA-D0 (100 nm at 0.2, 2, and 20 Å s$^{-1}$)/HAT-CN (5 nm)/Au (50 nm).

**Fig. S9** Thickness changes of as-deposited BPBPA-D0 films fabricated at deposition rates of 0.2, 2, and 20 Å s$^{-1}$ determined by *in situ* ellipsometry during a heating-cooling cycle. To compare the relative film densities of the as-deposited films, the thicknesses at 30 °C after cooling were used as the standards for normalization. The thicknesses of the as-deposited films are ~2% smaller than those of the films after cooling, but there was not a substantial difference (<0.1%) in the thickness of the as-deposited films fabricated at the different deposition rates.
Fig. S10 XRR patterns of BPBPA-D0 films deposited on a Si(100) substrate at deposition rates of (a) 0.2, (b) 2, and (c) 20 Å s\(^{-1}\). The analytical results of the thickness and film density are (a) 98.6 nm and 1.135 g/cm\(^3\), (b) 98.7 nm and 1.133 g/cm\(^3\), and (c) 97.9 nm and 1.138 g cm\(^{-3}\).

Fig. S11 Distribution of the HOMO of the BPBPA molecule obtained by DFT B3LYP/6-31G(d) calculation.
Fig. S12 $^1$H-NMR spectra of (a) BPBPA-D1 and (b) D2.