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Electronic supplementary information for

Synthesis of low-bandgap small molecules by extending the π -conjugation of the

termini in quinoidal compounds

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1. Instruments

¹H NMR and ¹³C NMR spectra were measured on a Bruker 400-MHz spectrometer at 400 and 100 MHz, respectively, in 1,1,2,2-tetrachloroethane- d_2 (C₂D₂Cl₄) or chloroform-d (CDCl₃) at room temperature. Matrix-assisted laser desorption ionization time-of-light (MALDI-TOF) mass spectra were recorded on a Bruker/AutoflexIII Smartbean MALDI mass spectrometer with 2-[(2E)-3-(4-tertbuthylphenyl)-2-methylprop-2-enylidene]malononotrile (DCTB) as the matrix in a reflection mode. UV-vis-NIR absorption spectra were recorded on a Shimadzu UV-3600 plus spectrometer. Solution spectra were measured in chloroform and thin-films were prepared by spin-coating their chloroform solutions (5 mg mL⁻¹) on the quartz substrates. Optical bandgap was calculated from the onset of thin-film absorption spectrum according to the equation: Eopt $g=1240/\lambda_{onset}$ eV. Solution cyclic voltammograms (CV) were measured in anhydrous dichloromethane using a CHI660 electrochemical analyzer with a three-electrode cell at a scan rate of 100 mV s⁻¹. Terabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 mol L⁻¹) was used as the supporting electrolyte. A Pt disk with 2 mm diameter, a Pt wire and a saturated calomel electrode (SCE) were used as working, counter and reference electrodes, respectively. The potential was calibrated against ferrocene/ferrocenium (Fc/Fc⁺) that was measured under the same conditions, which was 0.41 eV versus SCE. The highest molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels were calculated according to the equations: $E_{\text{HOMO}} = -(4.39 + \frac{E_{onset}}{onset}) \text{ eV}$ and $E_{LUMO} = -(4.39 + E_{onset}^{re})$ eV. Atomic force microscopy (AFM) measurements were carried out in tapping mode on a Bruker MultiMode 8 instrument. X-ray diffraction (XRD) of the thin films was measured with a Rigaku Smart Lab with Cu K_{α} source ($\lambda = 1.54056$ Å) in air. Density functional theory (DFT) optimized molecular geometries, DFT-calculated energy levels and frontier molecular orbital (FMO) distribution were conducted by Gaussian 09 with a hybrid B3LYP correlation functional and 6-31G (d, p) basis set. The branched alkyl side chains were replaced by methyl groups to simplify the calculations. To assign the absorption bands observed in the UV-vis-NIR spectra, time-dependent density functional theory (TD-DFT) calculations were performed on the optimized geometries using Gaussian 09 program at the B3LYP/6-31G (d, p) level. Natural orbital occupation number (NOON) calculations were done by spin unrestricted UCAM-B3LYP/ 6-31G(d,p) method and the diradical character (y) was calculated according to Yamaguchi's scheme: y = 1 - $(2T/(1 + T^2))$, and T = (nHOMO – nLUMO)/2 (nHOMO is the occupation number of the HOMO, nLUMO is the occupation number of the LUMO). The charge transfer integrals for the molecular dimer extracted from the experimental crystal structures were calculated at M06-2X/Def2-SVP level in the CT module of NWchem package.

2. Organic thin-film transistors (OTFTs) fabrication and measurements.

Top-gate/bottom-contact (TG/BC) OTFT devices were fabricated on silicon wafers with a 300 nm thick SiO₂. The substrate was first cleaned with deionized water, acetone and isopropanol in an ultrasonic bath and then dried under a nitrogen flow, followed by heating at 120 °C for 10 min. Subsequently, gold souce/drain electrodes were prepared by vacuum deposition through a shadow mask (W = 5600 μ m, L = 50 μ m). The pre-patterned substrates were treated with Ba(OH)₂ (2 mg/mL in methanol solution) by spin-coating with 5000 rpm for 90s, followed by annealing at 60 °C for 5 min. The semiconductor thin-films were deposited by spin-coating the chloroform solution (10 mg/mL) in an argon-filled glovebox with 5000 rpm for 90s. Then the thin-films were annealed at 40 °C for 10 min to remove the residual solvent. As the dielectric, CYTOP was spin-coated at 2000 rpm for 2 min and annealed at 100 °C for 40 min. Finally, Al (~80 nm) was vacuum-evaporated as the device gate. OTFT devices were measured under ambient conditions with Keysight B1500A source/measure units. Mobility was calculated in saturation regime by using the equation: Isat $DS = (\mu C_i W/2L)(V_{GS}-V_T)^2$, in which Isat DS is the drain-source current, μ is the mobility, C_i is the capacitance per unit area of the dielectric layer, V_{GS} and V_T are the gate voltage and threshold voltage, respectively.

3. Supplementary Data



Figure S1. ¹H NMR spectrum of 2a (400 MHz, CDCl₃).



Figure S2. ¹H NMR spectrum of 2b (400 MHz, CDCl₃).



Figure S3. ¹H NMR spectrum of 7 (400 MHz, CDCl₃).

Figure S4. ¹H NMR spectrum of QIDT-H (400 MHz, C₂D₂Cl₄).

Figure S5. ¹³C NMR spectrum of QIDT-H (100 MHz, CDCl₃).

Figure S6. MALDI-TOF mass spectrum of QIDT-H.

Figure S7. ¹H NMR spectrum of QIDT-4F (400 MHz, C₂D₂Cl₄).

Figure S8. ¹³C NMR spectrum of QIDT-4F (100 MHz, CDCl₃).

Figure S9. MALDI-TOF mass spectrum of QIDT-4F.

Figure S10. ¹H NMR spectrum of QSiIDT-H (400 MHz, C₂D₂Cl₄).

Figure S11. ¹³C NMR spectrum of QSiIDT-H (100 MHz, CDCl₃).

Figure S12. MALDI-TOF mass spectrum of QSiIDT-H.

Figure S13. ¹H NMR spectrum of QSiIDT-4F (400 MHz, C₂D₂Cl₄).

Figure S14. ¹³C NMR spectrum of QSiIDT-4F (100 MHz, CDCl₃).

Figure S15. MALDI-TOF mass spectrum of QSiIDT-4F.

Figure S16. ¹H NMR spectrum of QIDTCN (400 MHz, C₂D₂Cl₄).

Figure S17. ¹³C NMR spectrum of QIDTCN (100 MHz, CDCl₃).

Figure S18. MALDI-TOF mass spectrum of QIDTCN.

Figure S19. Variable-time ¹H NMR spectrum of QIDT-H (400 MHz, C₂D₂Cl₄).

Figure S20. Variable-time ¹H NMR spectrum of QIDT-4F (400 MHz, C₂D₂Cl₄).

Figure S21. Variable-time ¹H NMR spectrum of QSiIDT-H (400 MHz, C₂D₂Cl₄).

Figure S22. Variable-time ¹H NMR spectrum of QSiIDT-4F (400 MHz, C₂D₂Cl₄).

Figure S23. The calculated transfer integrals of HOMO and LUMO between the stacked molecules.

Figure S24. DFT-calculated frontier molecular orbital distribution diagrams of QIDT-

H, QIDT-4F, QSiIDT-H and QSiIDT-4F.

Figure S25. Oscillator strength of HOMO to LUMO transitions for QIDT-H, QIDT-4F, QSiIDT-H, QSiIDT-4F and QIDTCN calculated by TD-DFT.

Compound	T _{Anneal.}	μ^{max} μ^{ave}	$V_{\mathrm{T}} [\mathrm{V}]^{\mathrm{c}}$	$I_{\rm on}/I_{\rm off}{}^{\rm d}$
	[°C]ª	· e (· e)		
		$[m cm^2 V^{-1} s^{-1}]$		
QIDT-H	40	$0.0042 \ (0.0037 \pm 0.00046)$	2.7 ± 1.1	~10 ³
	80	$0.0028 \ (0.0024 \pm 0.00036)$	1.2 ± 1.8	$\sim \! 10^4$
	120	$0.0013 \ (0.0011 \pm 0.00012)$	4.2 ± 3.6	$\sim \! 10^4$
	160	$0.0038 \ (0.0029 \pm 0.00071)$	1.3 ± 2.4	~10 ³
QIDT-4F	40	$0.020 \ (0.016 \pm 0.0032)$	4.3 ± 1.8	~10 ³
	80	$0.017(0.010 \pm 0.0054)$	6.0 ± 2.0	~10 ³
	120	$0.011 \ (0.0077 \pm 0.0035)$	3.2 ± 1.9	$\sim \! 10^4$
	160	$0.002(0.0010 \pm 0.0038)$	9.0 ± 1.1	$\sim \! 10^4$
QSiIDT-H	40	$0.0075 (0.0071 \pm 0.00045)$	4.9 ± 2.2	~10 ³
	80	$0.0051(0.0046 \pm 0.00049)$	3.2 ± 1.3	~103
	120	$0.0063(0.0059 \pm 0.00061)$	7.0 ± 1.7	~10 ³
	160	$0.0017(0.0013 \pm 0.00034)$	16.0 ± 2.4	$\sim \! 10^4$
QSiIDT-4F	40	$0.041 \ (0.036 \pm 0.0043)$	8.1 ± 1.6	~10 ³
	80	$0.028 \ (0.026 \pm 0.0014)$	2.4 ± 1.2	~10 ³
	120	$0.037 (0.033 \pm 0.0041)$	5.7 ± 2.3	~10 ³
	160	$0.0090 \ (0.0071 \pm 0.00097)$	7.9 ± 1.7	~104

 Table S1. The OTFT device parameters at different annealed temperatures.

^aAnnealing temperature. ^bThe values in parentheses are average mobilities and standard deviations of data from at least six devices. ^cThreshold voltage. ^dCurrent on/off ratio.

4. X-ray crystallography

The single crystals of compounds QIDT-H, QIDT-4F, QSiIDT-H and QSiIDT-4F were grown by diffusion of methanol into their toluene solutions. The data were collected on a "Bruker APEX-II CCD" diffractometer. In the Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation.

Identification code	QIDT-H	
Empirical formula	C58 H64 O4 S2	
Formula weight	889.21	
Temperature	169.96 K	
Wavelength	1.34139 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 11.528(7) \text{ Å} \qquad \Box = 94.882(16)^{\circ}.$	
	$b = 13.982(9) \text{ Å}$ $\Box = 99.758(15)^{\circ}.$	
	$c = 16.137(10) \text{ Å}$ $\Box = 103.958(13)^{\circ}.$	
Volume	2466(3) Å ³	
Z	2	
Density (calculated)	1.198 Mg/m ³	
Absorption coefficient	0 864 mm ⁻¹	
Aussiption coefficient	0.004 mm	
F(000)	952	
Crystal size	0.05 x 0.003 x 0.002 mm ³	
Theta range for data collection	3.505 to 54.729°.	
Index ranges	-12<=h<=14, -17<=k<=17, -19<=l<=15	
Reflections collected	19310	
ndependent reflections $8857 [R(int) = 0.1503]$		
Completeness to theta = 53.594°	96.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4486	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8857 / 26 / 581	
Goodness-of-fit on F ²	0.984	
Final R indices [I>2sigma(I)]	R1 = 0.1366, WR2 = 0.2801	
R indices (all data)	R1 = 0.3081, WR2 = 0.3687	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.716 and -0.429 e.Å ⁻³	

 Table S2. Crystal data and structure refinement for QIDT-H.

Identification code	QIDT-4F		
Empirical formula	C58 H60 F4 O4 S2		
Formula weight	961.18		
Temperature	173.0 K		
Wavelength	1.34139 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	a = 11.445(10) Å	$\Box = 83.65(3)^{\circ}.$	
	b = 15.379(13) Å	$\Box = 81.33(2)^{\circ}.$	
	c = 16.753(15) Å	$\Box = 79.31(2)^{\circ}.$	
Volume	2854(4) Å ³		
Z	2		
Density (calculated)	1.119 Mg/m ³		
Absorption coefficient	0.835 mm ⁻¹		
F(000)	1016		
Crystal size	0.08 x 0.02 x 0.01 mm	1 ³	
Theta range for data collection	3.307 to 54.875°.		
Index ranges	-13<=h<=13, -18<=k<	-13<=h<=13, -18<=k<=18, -15<=l<=20	
Reflections collected	22638		
Independent reflections	10382 [R(int) = 0.127	10382 [R(int) = 0.1275]	
Completeness to theta = 53.594°	96.7 %		
Absorption correction	Semi-empirical from e	Semi-empirical from equivalents	
Max. and min. transmission	0.7508 and 0.4575	0.7508 and 0.4575	
Refinement method	Full-matrix least-squa	Full-matrix least-squares on F ²	
Data / restraints / parameters	10382 / 145 / 617	10382 / 145 / 617	
Goodness-of-fit on F ²	0.962		
Final R indices [I>2sigma(I)]	R1 = 0.1498, wR2 = 0	R1 = 0.1498, wR2 = 0.3256	
R indices (all data)	R1 = 0.2224, wR2 = 0	R1 = 0.2224, $wR2 = 0.3694$	
Extinction coefficient	n/a	n/a	
Largest diff. peak and hole	1.140 and -0.739 e.Å ⁻	1.140 and -0.739 e.Å ⁻³	

 Table S3. Crystal data and structure refinement for QIDT-4F.

Identification code	QSiIDT-H		
Empirical formula	C56 H64 O4 S2 Si2		
Formula weight	921.37		
Temperature	173.0 K		
Wavelength	1.34139 Å		
Crystal system	Triclinic		
Space group	P-1		
Unit cell dimensions	$a = 16.1862(14) \text{ Å}$ $\Box = 64.092(5)^{\circ}.$		
	$b = 17.1480(12) \text{ Å}$ $\Box = 84.168(6)^{\circ}.$		
	$c = 17.4487(16) \text{ Å} \qquad \Box = 89.134(5)^{\circ}.$		
Volume	4331.5(6) Å ³		
Z	3		
Density (calculated)	1.060 Mg/m ³		
Absorption coefficient	0 996 mm ⁻¹		
F(000)	1476		
Crystal size	0.1 x 0.03 x 0.03 mm ³		
Theta range for data collection	3.397 to 55.378°.		
Index ranges	-19<=h<=19, -20<=k<=20, -21<=l<=20		
Reflections collected	63101		
Independent reflections	16486 [R(int) = 0.1649]		
Completeness to theta = 53.594°	99.4 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission0.7508 and 0.4740			
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	16486 / 270 / 867		
Goodness-of-fit on F ²	0.818		
Final R indices [I>2sigma(I)]	R1 = 0.1537, wR2 = 0.3566		
R indices (all data)	R1 = 0.2593, WR2 = 0.4328		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.909 and -0.516 e.Å ⁻³		

 Table S4. Crystal data and structure refinement for QSiIDT-H.

Table S5. Crystal data and structure refinement for QSiIDT-4F.

Identification code	OSiIDT-4F
	201121

Empirical formula	C28 H30 F2 O2 S Si		
Formula weight	496.67		
Temperature	193.02 K		
Wavelength	1.34139 Å		
Crystal system	Monoclinic		
Space group	P 1 21/n 1		
Unit cell dimensions	a = 15.4494(9) Å	□= 90°.	
	b = 5.8637(3) Å	$\Box = 93.615(4)^{\circ}.$	
	c = 28.4818(16) Å	$\Box = 90^{\circ}.$	
Volume	2575.1(2) Å ³		
Z	4		
Density (calculated)	1.281 Mg/m ³		
Absorption coefficient	1.216 mm ⁻¹		
F(000)	1048		
Crystal size	0.1 x 0.02 x 0.02 mm ³	0.1 x 0.02 x 0.02 mm ³	
Theta range for data collection	2.760 to 54.958°.		
Index ranges	-18<=h<=17, -7<=k<=7, -34<=l<=34		
Reflections collected	24964		
Independent reflections	4880 [R(int) = 0.1768]		
Completeness to theta = 53.594°	99.6 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.7508 and 0.5606		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	/ restraints / parameters 4880 / 28 / 309		
Goodness-of-fit on F ²	1.024		
Final R indices [I>2sigma(I)]	R1 = 0.0928, wR2 = 0.2214		
R indices (all data)	R1 = 0.1908, wR2 = 0.2818		
Extinction coefficient	n/a		
Largest diff. peak and hole	0.712 and -0.417 e.Å ⁻³		