Synthesis, Optoelectronic properties and Photovoltaic Performances of

Wide Band-Gap Copolymers Based on Dibenzosilole and Quinoxaline units,

Rivals to P3HT

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Figure S1. Emission spectra of PDBS-TQx, PDBS-TQxF and PDBS-TzQx (a) in solution in chloroform and (b) in thin film.

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TQx	TQxF-Br	TzQx-Br
$C_{40}H_{46}N_2S_4$	$C_{40}H_{42}Br_2F_2N_2S_4$	$C_{38}H_{42}Br_2N_4S_4$
0.869 x 0.614 x 0.451	0.457 x 0.057 x 0.043	0.727 x 0.628 x 0.013
Tetragonal	Triclinic	Triclinic
17.5664(3)	16.7687(11)	9.0551(6)
17.5664(3)	18.2589(12)	10.0299(7)
44.8654(11)	20.6070(12)	22.0044(12)
90.00	112.675(6)	91.596(5)
90.00	100.139(5)	97.865(5)
90.00	92.575(5)	105.823(6)
13844.4(5)	5686.5(7)	1900.2(2)
16	6	2
14 ₁ /a	P-1	P-1
1.311	1.536	1.473
0.307	2.401	2.386
3.180 - 30.506	3.215 - 26.372	3.230 - 30.508
21885	38407	21348
10530	22546	11488
0.0423	0.0686	0.0821
0.1014	0.1857	0.2292
0.1373	0.1659	0.2507
0.0556	0.0742	0.0870
0.1151	0.1218	0.1758
5824	2688	864
0.379/-0.478	1.323/-0.828	0.785/-0.772
150(2)	150(2)	150(2)
	TQx C ₄₀ H ₄₆ N ₂ S ₄ 0.869 x 0.614 x 0.451 Tetragonal 17.5664(3) 17.5664(3) 44.8654(11) 90.00 90.00 90.00 90.00 90.00 90.00 13844.4(5) 16 14 ₁ /a 1.311 0.307 3.180 - 30.506 21885 10530 0.0423 0.1014 0.1373 0.0556 0.1151 5824 0.379/-0.478 150(2)	TQxTQxF-BrC40H42Br2F2N2S4C40H42Br2F2N2S40.869 x 0.614 x 0.4510.457 x 0.057 x 0.043TetragonalTriclinic17.5664(3)16.7687(11)17.5664(3)18.2589(12)44.8654(11)20.6070(12)90.00112.675(6)90.00100.139(5)90.0092.575(5)13844.4(5)5686.5(7)166141/aP-11.3111.5360.3072.4013.180 - 30.5063.215 - 26.372218853840710530225460.04230.06860.10140.18570.13730.16590.05560.07420.11510.1218582426880.379/-0.4781.302/-0.828150(2)150(2)

 Table S1. Single crystal X-Ray diffraction table for monomers TQx, TQx-Br-TzQx-Br



Figure S2. Chemical structure and stacking types in solid state of the molecules TQx, TQxF-Br and TzQx-Br determined by single crystal X-Ray diffraction measurements.



Figure S3. a) Output characteristic of a PDBS-TQxF OFET device annealed at 140°C for 10 minutes with a gate voltage ranging from 0 to -60 V by step of -10 V and b) Hole mobilities of

the polymer PDBS-TQxF in OFET devices in linear and saturated regimes as a function of the annealing temperature.

Table S2. Photovoltaic properties of the devices based on PDBS-TQx:PC₇₁BM deposited in solution with various solvents and additives.

		Additive	Thickness	V _{oc}	J_{SC}		η
Active layer	Solvent		(nm)	(V)	(mA.cm ⁻²)	FF	(%)
PDBS-TQx : PC ₇₁ BM 1 : 2	o-DCB	3 % DIO	160	0.23	6.84	0.31	0.50
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	50	0.85	9.72	0.62	5.14
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	10 % Anisole	50	0.82	4.55	0.43	1.60
PDBS-TQx : PC ₇₁ BM 1 : 2	CB	10 % Anisole	50	0.83	8.14	0 5 9	3 87
	СВ	3% DIO	50			0.58	5.07



Figure S4. AFM images, topography, $3\mu m \times 3 \mu m$ of active layer made of: PDBS-TQx : PC₇₀BM 1:2 deposited in solution in chlorobenzene (a) and with additives such as 10 % anisole (b) and 3 % DIO (c).



Figure S5. Photovoltaic characteristics obtained with the blend PDBS-TQx:PC₇₁BM 1:2 according to the active layer thickness.

Table S3. Photovoltaic characteristics obtained with the blend PDBS-TQx:PC₇₁BM 1:2. ^aPCE average on five devices.

Active layer		A 1 1111	Thickness		J _{SC}		η	
	Solvent	Additive	(nm)	(V)	(mA.cm ⁻²)	FF	(%)	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	155	0.83	4.73	0.58	2.27	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	125	0.58	7.01	0.64	2.61	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	110	0.73	7.36	0.50	2.67	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	95	0.62	7.17	0.61	2.70	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	70	0.64	8.04	0.60	3.08	
PDBS-TQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	50	0.85	9.72	0.62	5.14 (ª4.93)	



Figure S6. *J*-V curves of the devices from PDBS-TQxF with PC₇₁BM deposited in solution in *p*-

xylene.



Figure S7. *J*-V curves of the devices from PDBS-TQxF with $PC_{71}BM$ deposited in solution in chlorobenzene (a) as cast and (b) after thermal annealing at 120 °C.

Table S4. Photovoltaic characteristics obtained with the blend PDBS-TQxF:PC₇₁BM 1:2. ^aPCE average on five devices.

	Thermal	Thicknoss	V		FF	2
Solvent	annealing	(nm)	v _{oc}	J_{SC} (mA cm ⁻²)		ц (%)
	(°C)	()	(•)	(m/t.em/)		(70)
<i>p</i> -xylene	_	60	0 77	2 36	0 47	0.85
+ 3 % DIO		00	0.77	2.50	0.47	0.05
<i>p</i> -xylene	00	60	0.68 2.86 0.	0 5 1	0.00	
+ 3 % DIO	90	80		2.80	0.51	0.99
CB + 3 % DIO	-	50	0.69	6.38	0.45	1.96
CB + 3 % DIO	120	50	0.68	6.58	0.49	2.20
CB + 3 % DIO	-	60	0.79	5.20	0.40	1.64
CB + 3 % DIO	120	60	0.71	5.83	0.44	1.83
		75	0.91	7.27 0.5	0.51	2.98
CB + 3 % DIO	-		0.01		0.51	(ª2.78)
CB + 3 % DIO	120	75	0.76	7.61	0.55	3.19
	Solvent <i>p</i> -xylene + 3 % DIO <i>p</i> -xylene + 3 % DIO CB + 3 % DIO	ThermalSolventannealing (°C) p -xylene- $+ 3 \%$ DIO- p -xylene 90 $+ 3 \%$ DIO-CB + 3 % DIO-CB + 3 % DIO120CB + 3 % DIO-CB + 3 % DIO-CB + 3 % DIO-CB + 3 % DIO120CB + 3 % DIO-CB + 3 % DIO120CB + 3 % DIO-CB + 3 % DIO120	Thermal SolventThermal annealing (°C)Thickness (nm) p -xylene $+ 3 \% DIO-60p-xylenep-xylene9060p-xylene9060f 3 % DIO-50CB + 3 % DIO-50CB + 3 % DIO-60CB + 3 % DIO-60CB + 3 % DIO-60CB + 3 % DIO-75CB + 3 % DIO-75$	Thermal SolventThermal annealing (°C)Thickness V_{oc} (mm) p -xylene $+ 3 \% DIO-600.77r + 3 \% DIO 600.77p-xylene90600.68r + 3 \% DIO-500.69CB + 3 % DIO-500.68CB + 3 % DIO120500.68CB + 3 % DIO-600.79CB + 3 % DIO120600.71CB + 3 % DIO-750.81CB + 3 % DIO120750.76$	Thermal annealing $(^{\circ}C)$ Thickness (nm) V_{0C} J_{5C} $(mA.cm^{-2})$ (W) p -xylene $+ 3 \% DIO$ $ 60$ 0.77 2.36 p -xylene p -xylene $+ 3 \% DIO$ $ 60$ 0.77 2.36 p -xylene $+ 3 \% DIO$ $ 60$ 0.68 2.86 F 90 60 0.68 2.86 $CB + 3 \% DIO$ $ 50$ 0.68 6.58 $CB + 3 \% DIO$ 120 50 0.68 6.58 $CB + 3 \% DIO$ 120 60 0.71 5.83 $CB + 3 \% DIO$ $ 75$ 0.81 7.27 $CB + 3 \% DIO$ 120 75 0.76 7.61	Thermal annealingThickness V_{0c} J_{5c} FF Solventannealing (°C)(mm)(V)(mA.cm ⁻²) FF p -xylene p -xylene $ 60$ 0.77 2.36 0.47 p -xylene p -xylene 90 60 0.68 2.86 0.51 r 90 60 0.69 6.38 0.45 $CB + 3 \% DIO$ $ 50$ 0.69 6.38 0.45 $CB + 3 \% DIO$ 120 50 0.68 6.58 0.49 $CB + 3 \% DIO$ 120 60 0.71 5.83 0.44 $CB + 3 \% DIO$ $ 75$ 0.81 7.27 0.51 $CB + 3 \% DIO$ $ 75$ 0.76 7.61 0.55

Table S5. Photovoltaic characteristics obtained with the blend PDBS-TzQx:PC₇₁BM. ^aPCE average on five devices.

Active layer	Solvent	Additive	Thickness	V _{oc}	J _{SC}		η
			(nm)	(V)	(mA.cm ⁻²)	FF	(%)
PDBS-TzQx : PC ₇₁ BM 1 : 2	CP		50	50 0.63 4.92	0.41	1.27	
	СВ	3 % DIO	50		4.92	0.41	(°1.03)
PDBS-TzQx : PC ₇₁ BM 1 : 2	СВ	3 % DIO	100	0.54	4.09	0.40	0.89
PDBS-TzQx : PC ₇₁ BM 1 : 3	СВ	3 % DIO	85	0.54	2.93	0.43	0.67