Supplementary Information

Synthesis alternating D-A1-D-A2 terpolymers comprising two electron-deficient moieties, quinoxaline and benzothiadiazole units for photovoltaic application

M. L. Keshtov^{a*}, A.R. Khokhlov^a, S. A. Kuklin^a, F.C. Chen^b, A. Y. Nikolaev^a, E. N. Koukaras^{c,d} G. D. Sharma^{e*}

^aInstitute of Organoelement Compounds of the Russian Academy of Sciences, Vavilova St., 28, 119991 Moscow, Russian Federation

^bDepartment of Photonics, National Chiao Tung University, 1001 University Road, Hsinchu,

Taipei 30010, Taiwan

^cNanotechnology and Advanced Materials Laboratory, Department of Chemical Engineering, University of Patras, Patras, 26500 GR, Greece

^dMolecular Engineering Laboratory, Department of Physics, University of Patras, Patras, 26500 GR, Greece

^eDepartment of Physics, The LNM Institute of Information Technology, Jamdoli, Jaipur (Rajasthan) 302031, India

Technical Details of the Computations

We have additionally performed a theoretical study on the P1 and P2 molecular structures within the framework of density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The initial geometry optimization calculations were performed employing the gradient corrected functional PBE [1] of Perdew, Burke and Ernzerhof. The def-SVP basis set [2] was used for all of the calculations. At this stage of the calculations, to increase the computational efficiency (without loss in accuracy), the resolution of the identity method [3] was used for the treatment of the two-electron integrals. Subsequent geometry optimizations were further performed using the hybrid exchangecorrelation functional B3LYP [4] as well as Truhlar's meta-hybrid exchange-correlation functional M06 [5], and the same basis set. Tight convergence criteria were placed for the SCF energy (up to 10-7 Eh) and the one-electron density (rms of the density matrix up to 10–8) as well as for the norm of the Cartesian gradient (residual forces both average and maximum smaller than 1.5x10-5 a.u.) and residual displacements (both average and maximum smaller than 6x10-5 a.u.). Solvent effects were included for chloroform (CF) using the integral equation formalism variant of the Polarizable Continuum Model (IEFPCM), as implemented in the Gaussian package [6]. TD-DFT excited state calculations were performed to calculate the optical gaps of P1 and P2 using the same functionals and basis set on the corresponding ground state structures. The UV/Vis spectra were calculated using the B3LYP and M06 functionals. The first round of geometry optimization was performed using the Turbomole package [7]. All of the follow up calculations were performed using the Gaussian package [6].

The first round of calculations was the geometry optimizations of the P1 and P2 structures. To increase the computational efficiency, the alkyl groups were truncated to ethyl groups. Vibrational analysis on all of the optimized structures did not reveal any vibrational modes with imaginary eigenfrequencies, i.e. the final optimized structures are true local (if not global) minima.

In addition to the B3LYP functional we have also performed our calculations employing the M06 functional. The M06 meta-hybrid functional was chosen since it provides leveled performance over

transition types [8, 9]. We provide results using all three functionals, which can additionally be used for comparison with the literature.

The computed UV/Visual spectra have been produced by convoluting Gaussian functions with HWHM = 0.16 eV centered at the excitation wavenumbers.

References

- 1. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865
- 2. A. Schafer, H. Horn and R. Ahlrichs, J. Chem. Phys. 1992, 97, 2571.
- 3. K. Eichkorn, O. Treutler, H. Öhm, M. Häser and R. Ahlrichs, Chem. Phys. Lett. 1995, 240, 283.

4. (a) A. D. Becke, J. Chem. Phys. 1993, 98, 5648; (b) C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 1988, 37, 785

4. Y. Zhao and D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215

 Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 03, revision C.01; Gaussian, Inc.: Wallingford CT, 2004.

7. TURBOMOLE (version 5.6); Universitat Karlsruhe, 2000.

8. D. Jacquemin, E. A. Perpète, I. Ciofini, Adamo, R. Valero, Y. Zhao and D. G. Truhlar, J. Chem. Theory Comput. 2010, 6, 2071

9. S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, M. Nature Chem. 2014, 6, 242.



Figure S1 ¹HNMR spectra of copolymers (a) **P1** and (b) and **P2**



Figure S2 Near frontier orbitals of (a) **P1** and (b) **P2**, involved in transitions that contribute to the first few excitations.



Figure S3 Total and partial density of states of (a) P1 and (b) P2 (calculated using the M06 functional).



Figure S4. Theoretical UV/Vis absorption spectrum **P1** and **P2** (calculated using the B3LYP functional).

Table S1

Electronic excitations of P1 (with non-negligible oscillator strengths, f), and the corresponding major	or
contributions. Calculated using the M06 functional (and CF for solvent)	

No.	Wavelength (nm)	f	Main Contributions
1	575	0.6974	H→L (98%)
2	466	0.081	H→L+1 (95%)
3	435	0.1628	H − 1→L (81%)
			H−1→L+1 (11%)
5	389	0.096	H−1→L+1 (44%)
			H − 2→L (31%)
			H−1→L (14%)
6	374	0.1735	H→L+2 (78%)
			H−1→L+1 (14%)
8	356	0.4648	H − 1→L+2 (72%)
			H−2→L+1 (14%)
9	343	0.0522	H−2→L+1 (35%)
			H−3→L (33%)
			H−1→L+2 (16%)
10	338	0.2278	H→L+3 (49%)
	226		H−2→L+1 (15%)
11	336	0.2127	H−5→L (36%)
			H→L+3 (30%)
			$H-4 \rightarrow L(13\%)$
12	221	0 1 2 0 2	H−b→L (11%)
12	551	0.1202	⊓−3→L (32%) H_2 →L±1 (20%)
			H=2→L+1 (29%)
15	312	0 0309	H−3→L (20%)
16	207	0.0303	$11 \ 3 \rightarrow 1 \ 1 \ (30\%)$
10	507	0.0271	$H=3 \rightarrow L+1 (21\%)$
			⊓−4→L (14%) H_6 \L+1 (10%)
17	302	0 1255	H=8→L+1 (10%)
17	502	0.1235	H−2→L+2 (12%)
			H→L+4 (12%)
18	300	0.136	H→L+4 (32%)
			H−9→L (20%)
			, H−8→L (11%)
20	298	0.1107	H–2→L+2 (46%)
			H−8→L (18%)
21	295	0.0934	H−3→L+2 (24%)
			H−5→L+2 (12%)
			H − 4→L+2 (10%)
22	289	0.019	H − 6→L+1 (39%)
			H − 4→L+1 (19%)
			H–4→L (10%)
24	286	0.0337	H−9→L (44%)
_			H–>L+4 (20%)
25	284	0.0221	H–10→L (51%)
			H−1→L+3 (12%)
20	272	0 4 6 4 7	H→L+4 (20%)
28	272	0.1647	H−3→L+2 (34%)
			H−11→L (24%)

Table S2

Electronic	excitations	of P2	(with :	non-negli	gible	oscillator	strengths,	<i>f</i>),	and the	corresp	onding	major
contributio	ons. Calcula	ted usir	ng the	M06 func	tional	(and CF	for solven	t).				

No.	Wavelength (nm)	f	Main Contributions
1	731	1.17	H→L (95%)
2	617	0.11	H→L+1 (95%)
3	502	0.18	H−1→L (90%)
4	468	0.21	H−2→L (48%)
			H − 1→L+1 (38%)
5	447	0.08	H − 2→L (15%)
			H − 1→L+1 (39%)
			H→L+2 (36%)
6	436	0.35	H−2→L (14%)
			H − 1→L+1 (17%)
			H→L+2 (55%)
7	403	0.54	H − 2→L (11%)
			H − 2→L+1 (12%)
			H→L+3 (68%)
8	396	0.22	H − 2→L+1 (67%)
			H→L+3 (18%)
11	361	0.23	H − 4→L (58%)
			H − 4→L+1 (18%)
16	335	0.13	H−9→L (13%)
			H−2→L+2 (23%)
			H−1→L+2 (41%)
24	311	0.12	H→L+5 (66%)