Electronic Supplementary Information

The electron transfer rate of large TPA based compounds: a joint theoretical and electrochemical approach

Alessandra Degli Esposti[1], Valeria Fattori, Cristiana Sabatini, Giuseppe Casalbore-Miceli, Giancarlo Marconi

Istituto per la Sintesi Organica e la Fotoreattività (ISOF), CNR, via P. Gobetti, 101, I-40129 Bologna (Italy)

Fig.S1: HOMO electron density contouring drawn using MOLDEN:
G. Schaftenaar and J. H. Noordik, J. Comput.-Aided Mol. Design **14**, 123 (2000).

Table S1-S5: Significant bond lengths, planar and dihedral angles of NBDB, TAPC, MT-DATA, MPTAB, and MDTAB calculated using:

Gaussian 03, Revision B.05,
M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria,
M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven,
K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi,
V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega,
G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota,
R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao,
H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross,
C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev,
A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala,
K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg,
V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain,
O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari,
J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford,
J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz,
I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham,
C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill,
B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople,
Gaussian, Inc., Pittsburgh PA, 2003.

[1]Corresponding author *e-mail: alessandra.degliesposti@isof.cnr.it*

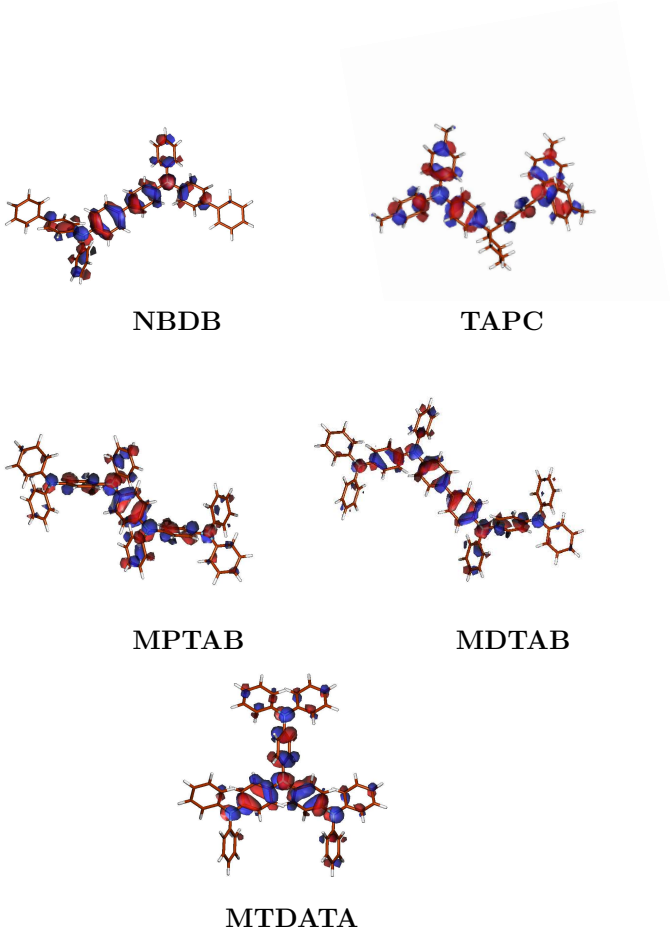
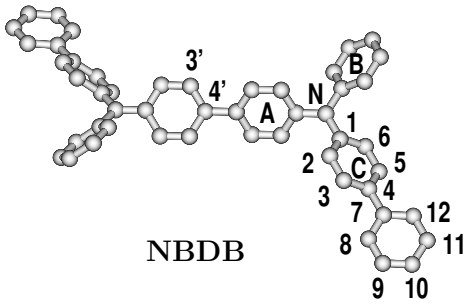


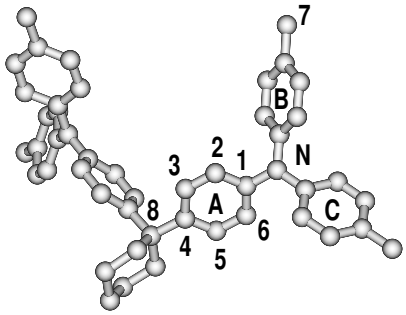
Figure S1: HOMO electron density contouring of NBDB, TAPC, MPTAB, MDTAB, and MTDATA.



NBDB

Table S1: NBDB: bond length (Å), planar and dihedral angles (*degrees*) of the neutral (**M**) and cationic ($\mathbf{M}^+$) species referred to the labeling in the figure.

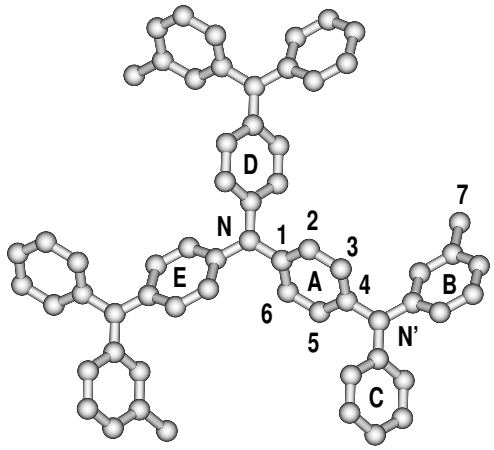
bond			*planar angle*			*dihedral angle*		
	M	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$
NC_1^A	1.420	1.392	$C_6^AC_1^AC_2^A$	118.4	118.0	$C_1^AC_1^BC_1^CN$	-0.3	0.1
$C_1^AC_2^A$	1.404	1.416	$C_1^AC_2^AC_3^A$	120.6	120.6	$C_2^AC_1^ANC_1^B$	-41.3	-28.1
$C_2^AC_3^A$	1.390	1.380	$C_2^AC_3^AC_4^A$	121.6	122.0	$C_2^BC_1^BNC_1^C$	-42.5	-47.9
$C_3^AC_4^A$	1.406	1.417	$C_3^AC_4^AC_5^A$	117.2	116.6	$C_3^AC_4^AC_{4'}C_{3'}$	34.8	22.1
$C_4^AC_{4'}$	1.481	1.459				$C_3^CC_4^CC_7C_8$	36.6	34.6
NC_1^B	1.423	1.431	$C_6^BC_1^BC_2^B$	119.0	120.1			
$C_1^BC_2^B$	1.404	1.402	$C_1^BC_2^BC_3^B$	120.3	119.7			
$C_2^BC_3^B$	1.394	1.393	$C_2^BC_3^BC_4^B$	120.6	120.4			
$C_3^BC_4^B$	1.397	1.397	$C_3^BC_4^BC_5^B$	119.3	119.8			
NC_1^C	1.419	1.424	$C_6^CC_1^CC_2^C$	118.3	119.0			
$C_1^CC_2^C$	1.405	1.405	$C_1^CC_2^CC_3^C$	120.6	120.1			
$C_2^CC_3^C$	1.390	1.389	$C_2^CC_3^CC_4^C$	121.6	121.5			
$C_3^CC_4^C$	1.406	1.408	$C_3^CC_4^CC_5^C$	117.2	117.5			
$C_4^CC_7$	1.483	1.480	$C_{12}C_7C_8$	118.0	118.3			
C_7C_8	1.406	1.406	$C_7C_8C_9$	121.0	120.8			
C_8C_9	1.394	1.393	$C_8C_9C_{10}$	120.3	120.2			
C_9C_{10}	1.396	1.396	$C_8C_9C_{11}$	119.4	119.6			



TAPC

Table S2: TAPC: bond length (Å), planar and dihedral angles (*degrees*) of the neutral (**M**) and cationic ($\mathbf{M}^+$) species referred to the labeling in the figure.

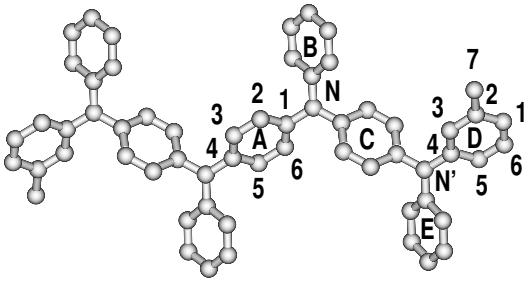
bond			*planar angle*			*dihedral angle*		
	M	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$
NC_1^A	1.420	1.406	$C_6^AC_1^AC_2^A$	118.0	118.3	$C_1^AC_1^BC_1^CN$	0.0	0.1
$C_1^AC_2^A$	1.400	1.411	$C_1^AC_2^AC_3^A$	120.7	120.3	$C_2^AC_1^ANC_1^B$	41.4	32.4
$C_2^AC_3^A$	1.395	1.384	$C_2^AC_3^AC_4^A$	122.1	122.1	$C_6^AC_1^ANC_1^C$	41.9	32.6
$C_3^AC_4^A$	1.402	1.411	$C_3^AC_4^AC_5^A$	116.4	116.9	$C_2^BC_1^BNC_1^C$	41.8	41.7
$C_4^AC_5^A$	1.406	1.406	$C_4^AC_5^AC_6^A$	122.2	121.8			
$C_5^AC_6^A$	1.390	1.390	$C_5^AC_6^AC_1^A$	120.6	120.5			
$C_6^AC_1^A$	1.404	1.408						
$C_4^AC_8$	1.546	1.542						
$NC_1^{B,C}$	1.422	1.422	$C_6^{B,C}C_1^{B,C}C_2^{B,C}$	118.4	119.2			
$C_1^{B,C}C_2^{B,C}$	1.404	1.405	$C_1^{B,C}C_2^{B,C}C_3^{B,C}$	120.5	120.0			
$C_2^{B,C}C_3^{B,C}$	1.393	1.390	$C_2^{B,C}C_3^{B,C}C_4^{B,C}$	121.6	121.5			
$C_3^{B,C}C_4^{B,C}$	1.401	1.404	$C_3^{B,C}C_4^{B,C}C_5^{B,C}$	117.5	117.8			
$C_4^{B,C}C_7^{B,C}$	1.511	1.508						



MTDATA

Table S3: MTDATA: bond length (Å), planar and dihedral angles (*degrees*) of the neutral (**M**) and cationic ($\mathbf{M}^+$) species referred to the labeling in the figure.

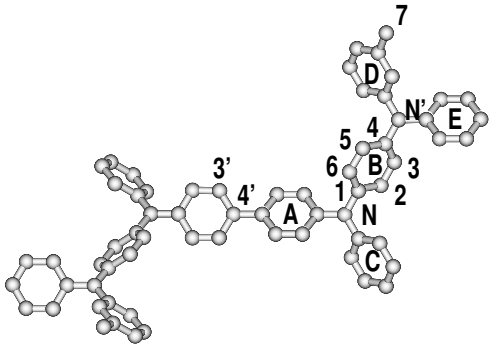
bond			*planar angle*			*dihedral angle*		
	M	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$
NC_1^A	1.421	1.410	$C_6^AC_1^AC_2^A$	118.3	118.4	$C_1^AC_1^DC_1^EN$	-0.1	0.0
$C_1^AC_2^A$	1.404	1.409	$C_1^AC_2^AC_3^A$	120.8	120.9	$C_1^AC_1^BC_1^CN'$	0.2	0.0
$C_2^AC_3^A$	1.390	1.382	$C_2^AC_3^AC_4^A$	120.9	121.0	$C_2^AC_1^ANC_1^D$	41.9	39.1
$C_3^AC_4^A$	1.404	1.416	$C_3^AC_4^AC_5^A$	118.3	117.8	$C_3^AC_4^AN'C_1^B$	-43.9	-25.0
C_4^AN'	1.422	1.392				$C_3^BC_1^BN'C_1^C$	-41.6	-50.4
						$C_3^CC_1^CN'C_1^A$	-39.4	-51.1
$C_4^{B,C}N'$	1.421	1.433	$C_6^{B,C}C_1^{B,C}C_2^{B,C}$	119.2	119.9			
$C_1^{B,C}C_2^{B,C}$	1.405	1.402	$C_1^{B,C}C_2^{B,C}C_3^{B,C}$	120.6	120.3			
$C_2^{B,C}C_3^{B,C}$	1.393	1.394	$C_2^{B,C}C_3^{B,C}C_4^{B,C}$	120.3	119.9			
$C_3^{B,C}C_4^{B,C}$	1.396	1.397	$C_3^{B,C}C_4^{B,C}C_5^{B,C}$	118.9	119.8			
$C_5^BC_7^B$	1.512	1.511						



MPTAB

Table S4: MPTAB: bond length (Å), planar and dihedral angles (*degrees*) of the neutral (**M**) and cationic ($\mathbf{M}^+$) species referred to the labeling in the figure.

bond			*planar angle*			*dihedral angle*		
	M	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$
NC_1^A	1.421	1.400	$C_6^AC_1^AC_2^A$	118.3	118.1	$C_1^AC_1^BC_1^CN$	0.2	-0.3
$C_1^AC_2^A$	1.405	1.414	$C_1^AC_2^AC_3^A$	120.8	121.0	$C_1^CC_1^DC_1^EN'$	0.3	-0.8
$C_2^AC_3^A$	1.391	1.381	$C_2^AC_3^AC_4^A$	120.8	121.0	$C_2^AC_1^ANC_1^B$	43.3	31.9
$C_3^AC_4^A$	1.404	1.414	$C_3^AC_4^AC_5^A$	118.3	118.1	$C_2^BC_1^BNC_1^C$	39.7	48.7
						$C_2^CC_1^CNC_1^A$	42.4	39.8
C_1^BN	1.420	1.432	$C_6^BC_1^BC_2^B$	118.8	119.8	$C_3^CC_4^CN'C_1^E$	-44.4	-26.3
$C_1^BC_2^B$	1.405	1.402	$C_1^BC_2^BC_3^B$	120.4	119.8	$C_3^DC_4^DN'C_1^C$	-41.1	-49.0
$C_2^BC_3^B$	1.393	1.393	$C_2^BC_3^BC_4^B$	120.7	120.4	$C_3^EC_4^EN'C_1^D$	-39.4	-48.1
$C_3^BC_4^B$	1.396	1.397	$C_3^BC_4^BC_5^B$	119.1	119.8			
C_1^CN	1.422	1.415	$C_6^CC_1^CC_2^C$	118.3	118.4			
$C_1^CC_2^C$	1.404	1.408	$C_1^CC_2^CC_3^C$	120.8	120.9			
$C_2^CC_3^C$	1.391	1.384	$C_2^CC_3^CC_4^C$	120.8	121.0			
$C_3^CC_4^C$	1.404	1.414	$C_3^CC_4^CC_5^C$	118.3	117.9			
C_4^CN'	1.421	1.396						
C_4^DN'	1.422	1.431	$C_6^DC_1^DC_2^D$	120.2	120.7			
$C_1^DC_2^D$	1.400	1.397	$C_1^DC_2^DC_3^D$	118.8	118.4			
$C_2^DC_3^D$	1.400	1.394	$C_2^DC_3^DC_4^D$	121.4	121.0			
$C_3^DC_4^D$	1.402	1.402	$C_3^DC_4^DC_5^D$	119.0	119.9			
$C_2^DC_7^D$	1.512	1.511						
C_4^EN'	1.420	1.430	$C_6^EC_1^EC_2^E$	119.1	119.6			
$C_1^EC_2^E$	1.396	1.397	$C_1^EC_2^EC_3^E$	120.6	120.4			
$C_2^EC_3^E$	1.393	1.394	$C_2^EC_3^EC_4^E$	120.3	120.0			
$C_3^EC_4^E$	1.405	1.402	$C_3^EC_4^EC_5^E$	118.9	119.7			



MDTAB

Table S5: MDTAB: bond length (Å), planar and dihedral angles (*degrees*) of the neutral (**M**) and cationic ($\mathbf{M}^+$) species referred to the labeling in the figure.

bond			*planar angle*			*dihedral angle*		
	M	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$		**M**	$\mathbf{M}^+$
NC_1^A	1.419	1.406	$C_6^AC_1^AC_2^A$	118.3	118.2	$C_1^AC_1^BC_1^CN$	-0.2	0.0
$C_1^AC_2^A$	1.405	1.411	$C_1^AC_2^AC_3^A$	120.6	120.6	$C_1^BC_1^DC_1^EN'$	0.6	0.0
$C_2^AC_3^A$	1.390	1.385	$C_2^AC_3^AC_4^A$	121.7	121.8	$C_2^AC_1^ANC_1^B$	39.6	33.4
$C_3^AC_4^A$	1.406	1.412	$C_3^AC_4^AC_5^A$	117.1	116.9	$C_2^BC_1^BNC_1^C$	43.2	38.0
$C_4^AC_{4'}$	1.480	1.468				$C_2^CC_1^CNC_1^A$	41.6	49.2
						$C_3^BC_4^BN'C_1^E$	-43.7	-29.2
C_1^BN	1.422	1.413	$C_6^BC_1^BC_2^B$	118.4	118.3	$C_3^DC_4^DN'C_1^B$	-42.1	-47.5
$C_1^BC_2^B$	1.404	1.409	$C_1^BC_2^BC_3^B$	120.8	120.9	$C_3^EC_4^EN'C_1^D$	-40.5	-47.0
$C_2^BC_3^B$	1.390	1.384	$C_2^BC_3^BC_4^B$	120.8	120.9	$C_3^AC_4^AC_{3'}C_{4'}$	-33.9	-29.4
$C_3^BC_4^B$	1.404	1.413	$C_3^BC_4^BC_5^B$	118.4	118.0			
C_4^BN'	1.422	1.399						
C_1^CN	1.421	1.430	$C_6^CC_1^CC_2^C$	119.2	119.8			
$C_1^CC_2^C$	1.405	1.402	$C_1^CC_2^CC_3^C$	120.6	119.8			
$C_2^CC_3^C$	1.393	1.393	$C_2^CC_3^CC_4^C$	120.3	120.4			
$C_3^CC_4^C$	1.397	1.397	$C_3^CC_4^CC_5^C$	118.9	119.7			
C_4^DN'	1.422	1.428	$C_6^DC_1^DC_2^D$	120.3	120.7			
$C_1^DC_2^D$	1.397	1.397	$C_1^DC_2^DC_3^D$	118.7	118.5			
$C_2^DC_3^D$	1.391	1.393	$C_2^DC_3^DC_4^D$	121.3	121.0			
$C_3^DC_4^D$	1.405	1.397	$C_3^DC_4^DC_5^D$	119.0	119.8			
$C_6^DC_7^D$	1.512	1.511						
C_4^EN'	1.420	1.429	$C_6^EC_1^EC_2^E$	119.1	119.6			
$C_1^EC_2^E$	1.396	1.397	$C_1^EC_2^EC_3^E$	120.6	120.4			
$C_2^EC_3^E$	1.393	1.393	$C_2^EC_3^EC_4^E$	120.3	119.9			
$C_3^EC_4^E$	1.405	1.402	$C_3^EC_4^EC_5^E$	118.8	119.6			