Spectral and Intramolecular Charge Transfer Properties in Terminal Donor/Acceptor-Substituted all-*trans*-α,ω-Diphenylpolyenes and α,ω-Diphenylpolyynes

Xiaonan Ma, Linyin Yan, Xuefei Wang, Qianjin Guo*, and Andong Xia*

The State Key Laboratory of Molecular Reaction Dynamics, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China. and Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, P. R. China

Supplementary Information

S1. Performance of several DFT methods

As mentioned in the section of computational methods, the PBE0 functional was selected from several popular functionals. Three classed of DFT XC-functionals (As shown in Table S1) with 6-31G(d) basis set are examined here by comparing the TDDFT calculated UV-Vis absorption wavelength with the experimental values in literatures. In the first category, two GGAs named BP86[1-2] and PBE[3] are chosen, we have also picked up two popular *meta*-GGA: VSXC[4] and TPSS[5]. In the last category, seven hybrid-GGAs have been used: B3LYP (20%)[6-7], B3PW91 (20%)[6,8], mPW1PW91 (25%)[9], PBE0 (25%)[10], O3LYP (11.61%)[11-12], X3LYP (21%)[13], BHHLYP (50%)[14]. It is worth to note that the TDDFT calculations presented here were performed in vacuum due to the consideration of calculation efficiency, i.e. the solvent effects have not been considered. This approximation would induce principle error in some extent, but because the experimental data presented here are measured in non-polar medium (such as *n*-hexane and cyclohexane), the induced error due to solvent effect is also limited. Moreover, recent studies indicated that comparison for experimental values of electron affinity and ionization potential with DFT calculated data give reliable results in choosing the right DFT XC-functional.[15-16] Unfortunately, the electron affinity and ionization potential data of compounds involved in this work is not available in any database so far, therefore to compare the electronic absorption data may still be the best feasible way to choose the functional.

Table S1. Functionals Examined in the Present Work

	Type	HF%	ex / corr
BP86	GGA	0	B88 / P86
PBE	GGA	0	PBE / PBE
VSXC	*meta*-GGA	0	VSXC / VSXC
TPSS	*meta*-GGA	0	TPSS / TPSS
B3LYP	hybrid-GGA	20%	B3 / LYP
B3PW91	hybrid-GGA	20%	B3 / PW91
mPW1PW91	hybrid-GGA	25%	mPW / PW91
PBE0	hybrid-GGA	25%	PBE / PBE
O3LYP	hybrid-GGA	11.61%	OPTX / LYP
X3LYP	hybrid-GGA	21%	X / LYP
BHHLYP	hybrid-GGA	50%	B88 / LYP

Table S2. The TDDFT calculated UV-Vis absorption wavelength by different functionals and the corresponding experimental values collected from references.

	DPE	DPE	DPE	DPE	DPE	DPE	DPY 2-HH		DPY 4-HH		DPY 6-HH	
	1-pp	2-pp	3-pp	2-HH	4-HH	6-HH	1st	2nd	1st	2nd	1st	2nd
Exp.	378[a]	400[a]	412[a]	346[b]	395[b]	435[b]	324[c]	263[c]	390[c]	308[c]	460[c]	350[c]
BP86	452	499	547	371	455	537	366	215	479	315	594	381
PBE	452	500	547	370	454	536	365	214	477	314	591	380
VSXC	432	476	521	360	441	520	356	209	467	305	579	369
TPSS	439	485	531	363	445	524	359	211	469	308	581	373
B3LYP	390	427	464	346	418	486	342	221	446	290	543	345
B3PW91	390	428	464	345	417	475	340	220	443	289	540	343
mPW1PW91	379	414	449	339	409	474	335	217	436	284	529	336
PBE0	379	414	449	339	409	473	334	216	434	283	528	336
O3LYP	410	450	491	354	431	504	349	226	454	297	557	356
X3LYP	386	422	458	344	416	482	340	220	444	288	542	342
BHHLYP	339	367	395	319	377	429	320	211	419	265	507	307

a. From reference[14]; b. From reference[17]; c. From reference[18].

Table S2 includes all of the TDDFT calculation results of absorption wavelength and corresponding experimental values. The experimental values of absorption wavelength used here are the wavelength in the absorption maximum, which represents a mean value of the absorption band distribution.[19] As expected, the accuracy of calculation results in matching the experimental value strongly depends on the XC-functional used. The GGA and *meta*-GGA functional lead to quite poor accuracy in UV-Vis spectra and tend to provide significant red shift, although *meta*-GGA (TPSS and VSXC) give more accurate spectral data than BP86 and PBE. The spectral data calculated by seven hybrid-GGAs are more accurate than the GGA and meta-GGA, probably because adding more exact exchange fraction which tends to shift the transition energies to larger values. Among the seven hybrid-GGAs, mPW1PW91 and PBE0 show high and less system dependent accuracy of absorption wavelength for all the species calculated here. The BHHLYP functional capture the wavelength values of the first band of DPYs particularly well, while the performances for other species are less accurate and system dependent. On the other hand, in TDDFT calculations, the functionals with small orbital exchange fraction (such as PBE0, 25%) often favor zwitterionic-like states with strong CT character. On the contrary, functionals with large oribital exchange fraction (such as BHandHLYP, 50%) is more suitable to treat the neutral-base electronic excitation.[20] Meanwhile, the use of PBE0 was recently recommended for calculations of numerous organic chromophores.[21-22] Therefore, the PBE0 function could be recommended for the systems in this work as the best compromise. However, it is necessary to note that the electronic transition energies of CT states generally tend to be underestimated by the TDDFT calculations using XC-functionals independently of the functional and basis set chosen,[19] the agreement with the corresponding experimental values decreases when the conjugation is extended (as shown in Table S2). Therefore, we used the second band rather than the CT band spectral data of DPYs to estimate the

ECL value in chapter 3.2. Accordingly, the ECL values estimated by the TDDFT calculated excitation energy are less accurate due to the principle error of the TDDFT methods mentioned previously, and therefore, the calculated ECL only can be tentatively considered as qualitative or semi-quantitative results. The more accurate quantitative result relies on the future application of high level excited state calculate methods (such as CASPT2 and MRCI) on such complex systems.

S2. TDDFT calculated UV-Vis absorption spectra of DPE and DPY series.

The spectral line shape is calculated with the multiple Gaussian function related to the corresponding excitation energy and oscillator strength from the TD-PBE0 calculations. The UV-Vis spectra peak half-width at half height tentatively sets as 0.3 eV (2419.66 cm^{-1}). Because the UV-Vis spectra shape of DPE and PDY species is relative simple and clear, the value of peak width would not make significant influence to the analysis of spectra. The absorption wavelength of DPE and the first band of DPY is further fitted to estimate the effective conjugated length (ECL) value.

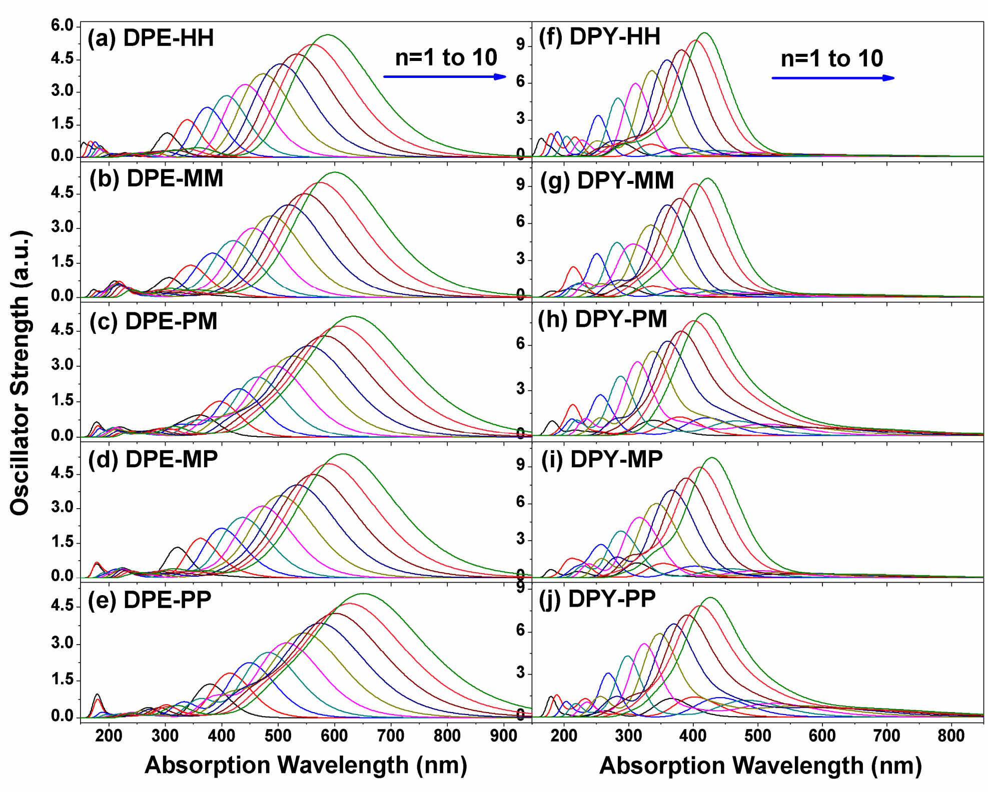


Figure S1. TDDFT calculated absorption spectra of DPE (the left column) and DPY (the right column) with different substituted mode and conjugated length.

S3. Charge Difference Density (CDD) and Transition Density (TD)

To identify the charge transfer and local excited character of states, we construct the visualized charge difference density (CDDs) and transition density (TDs) cube based on the CIS wavefunction used to calculate the electronic coupling. The CDDs ($\Delta\rho_{\mu\mu}$) and TDs ($\rho_{\mu 0}$) are given by:

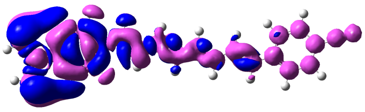
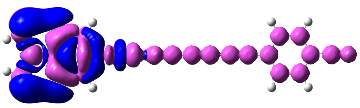
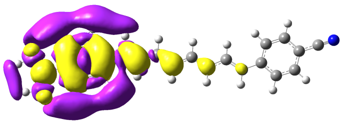
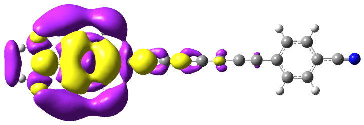
$$\Delta\rho_{\mu\mu}(\vec{r}) = \sum_{a,i,j} C_{\mu ai} C_{\mu aj} \varphi_i(\vec{r}) \varphi_j(\vec{r}) - \sum_{a,b,i} C_{\mu ai} C_{\mu bi} \varphi_a(\vec{r}) \varphi_b(\vec{r})$$

$$\rho_{\mu 0}(\vec{r}) = \sum_{a,i} C_{\mu ai} \varphi_a(\vec{r}) \varphi_i(\vec{r})$$

where $C_{\mu ai}$ represents the μth eigenvector of the Hamiltonian in the basis of the occupied Hartree-Fock molecular orbital $\varphi_i(r)$ and the unoccupied orbitals $\varphi_a(r)$. The CDD visualizes the difference in electron density upon electronic excitation between two electronic states (in this work between ground states and singlet excited states). The TD is a representation of the transition dipole moment and indicates the excitation regions of the molecule which are involved in electronic transition.[23-24]

To calculate the electronic coupling values, the CT and LE states should be identified firstly. The state characteristic of the CT state is easy to be identified, because the CT state localizes in the lowest singlet excited state with the simplex transition component from HOMO to LUMO. The LE states are deduced from the charge difference density (CDD) and transition density (TD) representation. As an example, Table 5 shows the CDD and TD representations of the LE states of the substituted DPE and DPY (n=6). The unbalanced distribution of TD representation of LE state indicates that the excitation is mainly localized in donor moiety, the acceptor moiety is not involved during photoexcitation. The corresponding CDD representation indicates that the charge density in acceptor moiety is exactly unchanged during the photoexcitation process, which is the typical characteristic of donor local excited state.

Table S3. CDD and TD Examples of LE State of DPE and DPY.

	DPE LE state	DPY LE state
TD		
CDD		

S4. The CIS-GMH calculated electronic coupling values.

The CIS-GMH calculated electronic coupling values (with the unit of eV) involved in electronic transfer rate and the corresponding donor-acceptor distance (with the unit of Å) values are listed in Table S5. In this work, the donor-acceptor distance is defined as the nitrogen atom in dimethylamine group to the carbon in cyano group.

Table S4. Calculated electronic coupling of charge transfer process and corresponding donor-acceptor distance

Electronic Coupling (H_{DA})×10^2/eV and D-A Distance (d)/Å in DPE								
	MM		PM		MP		PP	
	d	H_{DA}	d	H_{DA}	d	H_{DA}	d	H_{DA}
n=1	11.08	16.97	11.40	7.47	11.35	3.82	12.33	3.03
n=2	13.52	11.87	13.88	4.55	13.21	3.21	14.71	2.64
n=3	15.97	10.60	16.37	3.35	15.52	2.86	17.12	2.42
n=4	18.42	7.43	18.85	3.06	17.88	1.78	19.54	2.28
n=5	20.88	6.86	21.33	2.52	20.25	2.01	21.98	2.03
n=6	23.34	4.66	23.81	2.73	22.64	0.91	24.42	1.99
n=7	25.81	4.52	26.30	2.36	25.05	1.37	26.87	1.86
n=8	28.28	1.01	28.77	2.28	27.47	1.30	29.32	1.69
n=9	30.74	2.89	31.25	1.56	29.80	0.93	31.78	1.55
n=10	33.21	1.39	33.73	1.57	32.18	1.31	34.24	1.35
Electronic Coupling (H_{DA})×10^2/eV and D-A Distance (d)/Å in DPY								
	MM		PM		MP		PP	
	d	H_{DA}	d	H_{DA}	d	H_{DA}	d	H_{DA}
n=1	10.64	12.41	11.39	5.88	11.37	5.74	12.54	4.22
n=2	13.22	13.56	13.91	5.84	13.90	6.51	15.11	4.44
n=3	15.64	13.02	16.44	5.53	16.45	6.28	17.68	4.16
n=4	18.10	11.81	18.99	4.71	19.01	5.52	20.26	3.51
n=5	20.55	8.82	21.54	3.50	21.56	3.06	22.83	2.77
n=6	23.06	8.10	24.09	2.77	24.12	2.33	25.40	2.26
n=7	25.62	5.58	26.65	2.30	26.68	1.12	27.97	1.89
n=8	28.10	5.27	29.21	1.94	29.24	0.84	30.54	1.62
n=9	30.68	4.14	31.77	1.68	31.80	1.02	33.11	1.41
n=10	33.10	3.84	34.30	1.56	34.34	0.55	35.68	1.28

Reference

1. A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098-3100.
2. J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822-8824.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.
4. T. Van Voorhis and G. E. Scuseria, *J. Chem. Phys.*, 1998, **109**, 400-410.
5. J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Phys. Rev. Lett.*, 2003, **91**, 146401.
6. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648-5652.
7. C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.
8. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Kackson, M. A. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B*, 1992, **46**, 6671-6687.
9. C. Adamo and V. Barone, *Chem. Phys. Lett.*, 1997, **274**, 242-250.
10. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
11. J. Baker and P. Pulay, *J. Chem. Phys.*, 2002, **117**, 1441-1449.
12. X. Xu and W. A. Goddard III, *Proc. Natl. Acad. Sci. U.S.A.*, 2004, **101**, 2673-2677.
13. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372-1377.
14. H. El-Gezawy and W. Rettig, *Chem. Phys.*, 2006, **327**, 385-394.
15. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
16. Y. Zhao, N. E. Schultz and D. G. Truhlar, *J. Chem. Theor. Comput.*, 2006, **2**, 364-382.
17. T. Itoh, *J. Chem. Phys.*, 2005, **123**, 064302.
18. Y. Nagano, T. Ikoma, K. Akiyama and S. Tero-Kubota, *J. Am. Chem. Soc.*, 2003, **125**, 14103-14112.
19. J. Gierschner, J. Cornil and H. J. Egelhaaf, *Adv. Mater.*, 2007, **19**, 173-191.
20. C. Wu, S. Tretiak and V. Y. Chernyak, *Chem. Phys. Lett.*, 2007, **433**, 305-311.
21. J. Andzelm, B. C. Rinderspacher, A. Rawlett, J. Dougherty, R. Baer and N. Govind, *J. Chem. Theory Comput.*, 2009**,** **5**, 2835-2846.
22. D. Jacquemin, E. Perpete, G. E. Scuseria, I. Ciofini and C. Adamo, *J. Chem. Theory Comput.*, 2008, **4**, 123-135.
23. N. Persson, M. Sun, P. Kjellberg, T. Pullerits and O. Inganäs, *J. Chem. Phys.*, 2005, **123**, 204718.
24. M. Sun, *J. Chem. Phys.*, 2006, **124**, 054903.