Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Unusual binary aggregates of perylene bisimide revealed by their electronic transitions in helium nanodroplets and DFT calculations

S. Izadnia,[a] A. C. LaForge,[a] F. Stienkemeier,[a]* James Cheeseman,[b] Julien Bloino,[c] J. Cheramy,[d] Wolfgang Jäger,[d] Yunjie Xu[d]*

[a]*Physikalisches Institut, Universität Freiburg, Hermann-Herder-Str. 3, D-79104 Freiburg, Germany.*

[b]*Gaussian, Inc.*

[c]*Scuola Normale Superiore, Piazza dei Cavalieri, 7, 56126 Pisa, Italy.*

[d]*Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2*

* Corresponding Authors, Email: stienkemeier@uni-freiburg.de; yunjie.xu@ualberta.ca

Supplementary Information

Table of Contents

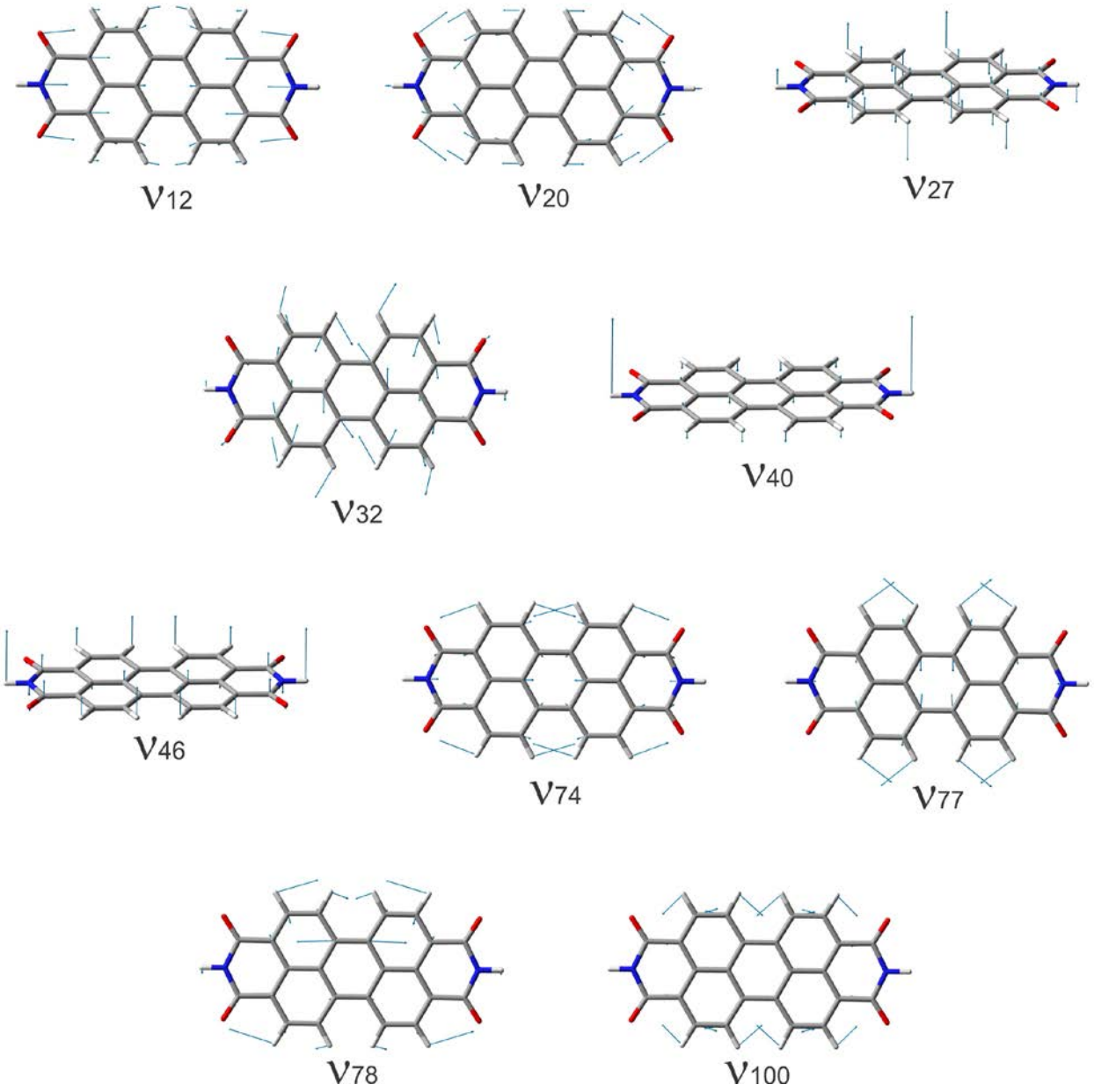

Figure S1. Vibrational motions of the ten fundamental bands which contribute significantly to the S0→S1 transition calculated at the CAM-B3LYP-D3BJ/6-311++G(2d,p) level.

Table S1. Calculated properties of the PBI monomer and dimers at the three levels of theory.[a]

APFD/6-311++G(2d,p)						
PBI monomer gs → ex1 AH 0-0 (cm^{-1})			18137			
PBI dimers	I τ_S(0)	I τ_S(70)	I τ_S(90)	I τ_S(90) _shifted	II τ_S(90)	III τ_S(90)
E_b (kcal/mol)[b]	9.04/8.75	9.82/9.44	9.78/9.27	11.29/10.53	10.84	/31.07
ΔE (kcal/mol)[c]	2.25/1.78	1.47/1.09	1.51/1.26	0.00/0.00	0.45	
top → top AH 0-0 (cm^{-1})[d]	18058/18056	/18035	18024/18019	/17963	18178	
Δ(0-0) (cm^{-1})[e]	-79/-80	/-102	-113/-118	/-174	+41	
bot → bot AH 0-0 (cm^{-1})[d]			17776/		18199	
Δ(0-0) (cm^{-1})[e]			-361/		+62	
B3LYP+GD3BJ/6-311++G(2d,p)						
PBI monomer gs → ex1 AH 0-0 (cm^{-1})			17670			
PBI dimers	I τ_S(0)	I τ_S(70)	I τ_S(90)	I τ_S(90) _shifted	II τ_S(90)	III τ_S(90)
E_b (kcal/mol)[b]	7.03/6.74		7.56/7.17	8.86/		/24.34
ΔE (kcal/mol)[c]						-
top → top AH 0-0 (cm^{-1})[d]	17591/17593		17573/17566			/17876
Δ(0-0) (cm^{-1})[e]	-79/-77		-97/-104			/+206
bot → bot AH 0-0 (cm^{-1})[d]						
Δ(0-0) (cm^{-1})[e]						
APFD/6-31G(d)						
PBI monomer gs → ex1 AH 0-0 (cm^{-1})			18745			
PBI dimers	I τ_S(0)	I τ_S(70)	I τ_S(90)	I τ_S(90) _shifted	II τ_S(90)	III τ_S(90)
E_b (kcal/mol)[b]	7.37	7.53	7.56	8.67	10.01	29.45
ΔE (kcal/mol)[c]	1.30	1.14	1.11	0.00		-
top → top AH 0-0 (cm^{-1})[d]	18665	18498	18628	18560		18709
Δ(0-0) (cm^{-1})[e]	-80	-247	-117	-185		-36
bot → bot AH 0-0 (cm^{-1})[d]						
Δ(0-0) (cm^{-1})[e]						

[a] Black colour indicates that the PBI dimers are fully relaxed, the bottom PBI ring is slightly bowed. The red colour indicates that the bottom PBI subunit is constrained as planar.

[b] The binding energy of the PBI dimer with the *ZPE* and *BSSE* correction.

[c] Relative energies compared to the most stable Type **I** PBI dimer calculated. Positive values mean less stable.

[d] See main text for the definition of top → top and bot → bot.

[e] The shift of the 0-0 band origin of the PBI dimer from that of the PBI monomer.

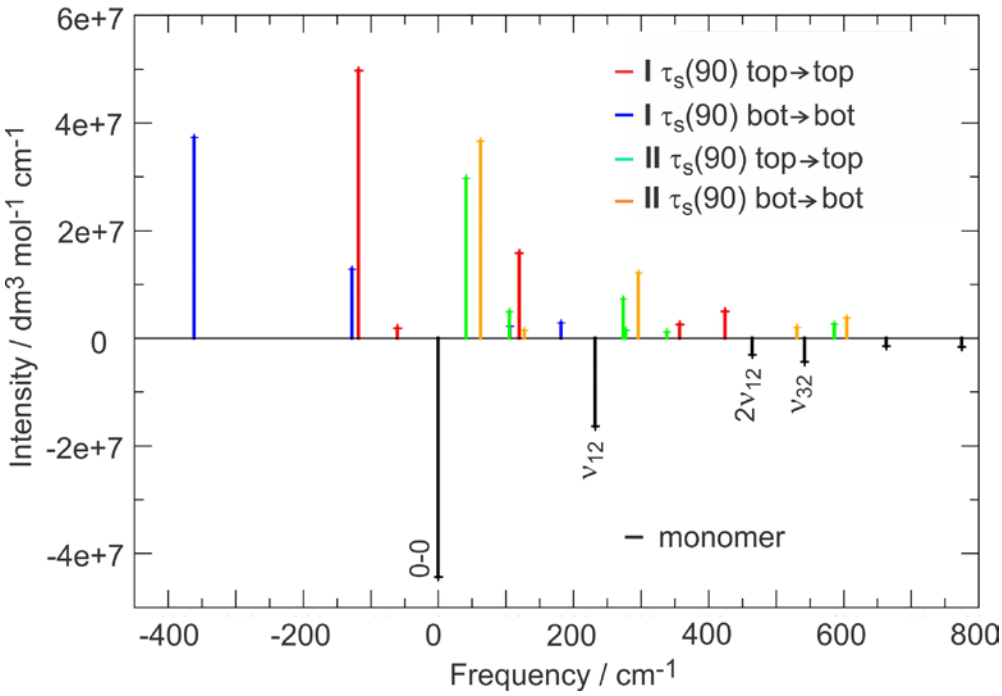

Figure S2. Simulated vibronic spectra of the top → top and bot → bot electronic transitions of of **I** $\tau_S(90)$ and **II** $\tau_S(90)$ PBI dimer structures (fully optimized) in comparison to that of the PBI monomer at the APFD/6-311++G(2d,p) level of theory.

Completion of references 31 and 32.

31. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**.

32. Gaussian Development Version, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, A. V. Marenich, M. Caricato, J. Bloino, B. G. Janesko, J. Zheng, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2020**.