2021 Literature report II

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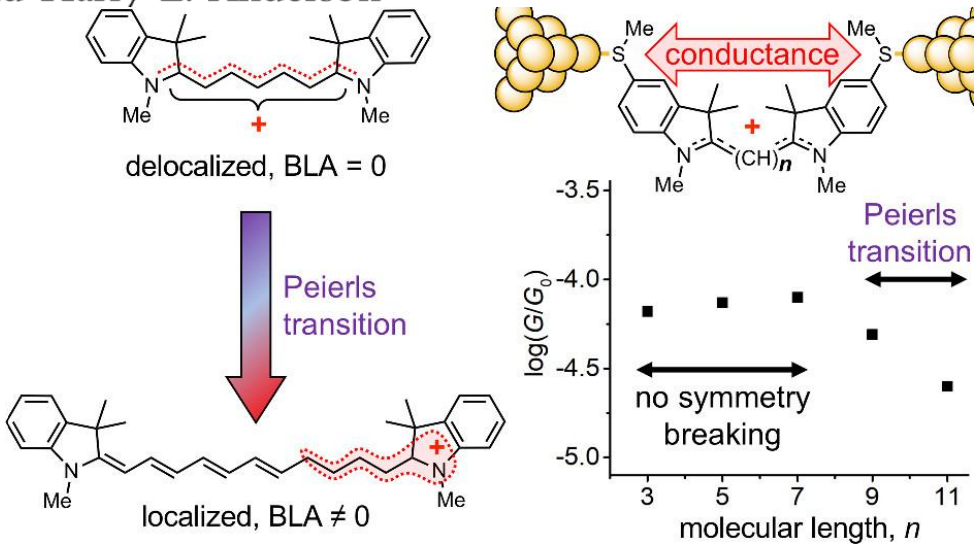
Article

A Peierls Transition in Long Polymethine Molecular Wires: Evolution of Molecular Geometry and Single-Molecule Conductance

Wenjun Xu,[▽] Edmund Leary,*[,▽] Sara Sangtarash, Michael Jirasek, M. Teresa González, Kirsten E. Christensen, Lydia Abellán Vicente, Nicolás Agraït, Simon J. Higgins, Richard J. Nichols, Colin J. Lambert, and Harry L. Anderson*



Author

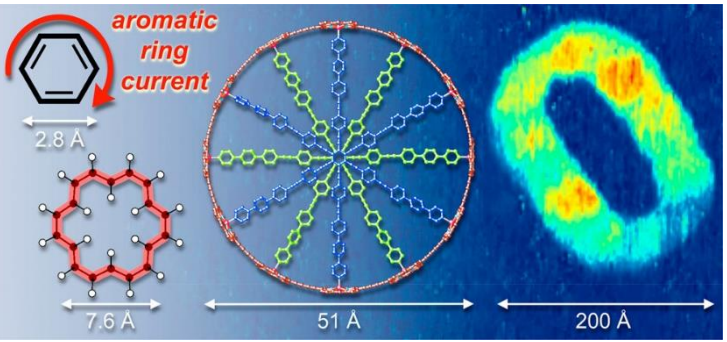
Harry L. Anderson

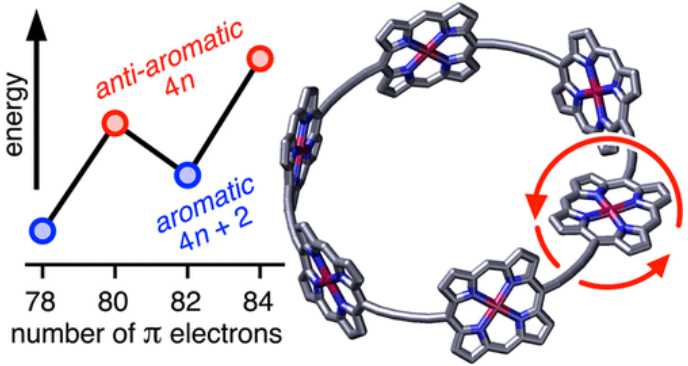
Completed PhD with Professor Jeremy Sanders at the University of Cambridge UK
Carried out postdoctoral work with Professor François Diederich at ETH Zurich, Switzerland
Led an independent research group in Oxford since 1995

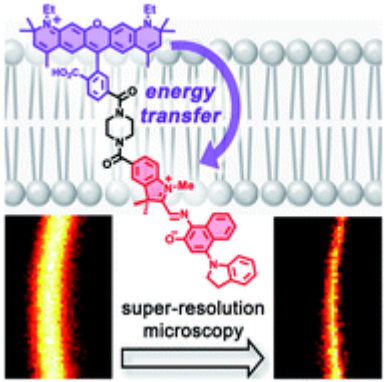
Research interest

Our research is in the areas of molecular materials synthesis, supramolecular chemistry, molecular recognition, polymers and dyes. We believe that a better understanding of the relationship between molecular structure, molecular function and macroscopic properties will give us the ability to build functional materials on the molecular scale.

Our work is directed towards the design and synthesis of functional molecular materials, and the elucidation of structures-property relationships.

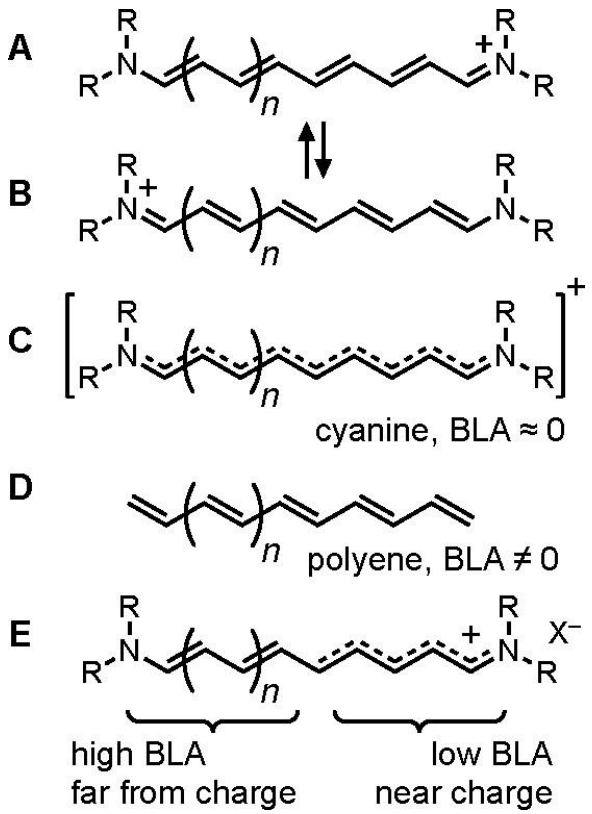


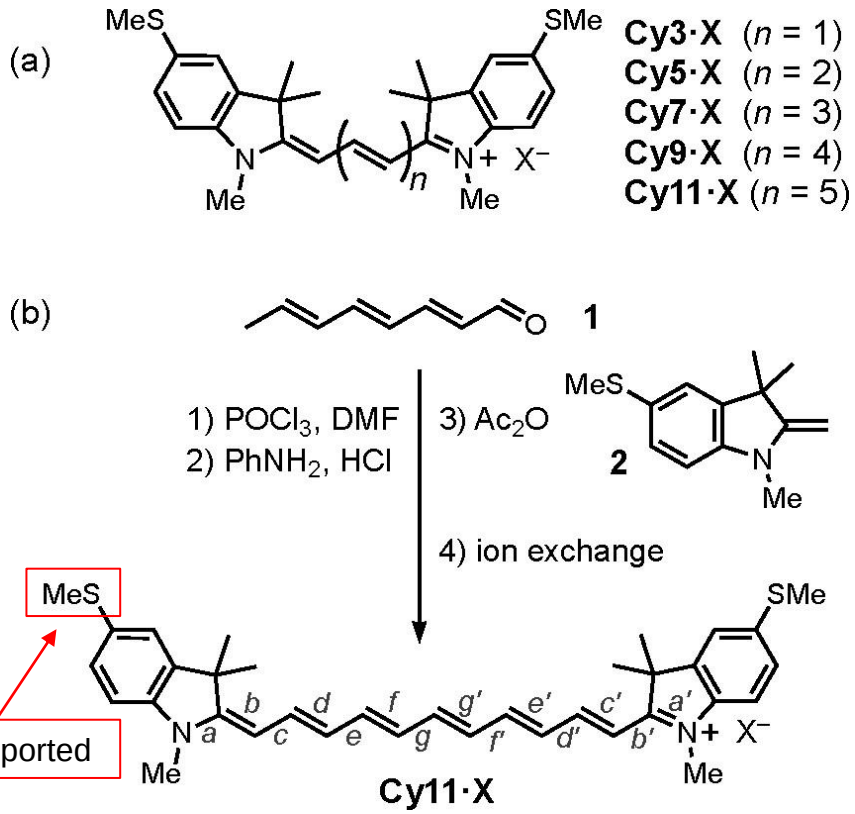




Edmund Leary	2011-2019 2019.08	Assistant Research Prof. (tenure track)	Universidad Autónoma de Madrid IMDEA Nanociencia Institute

Introduction



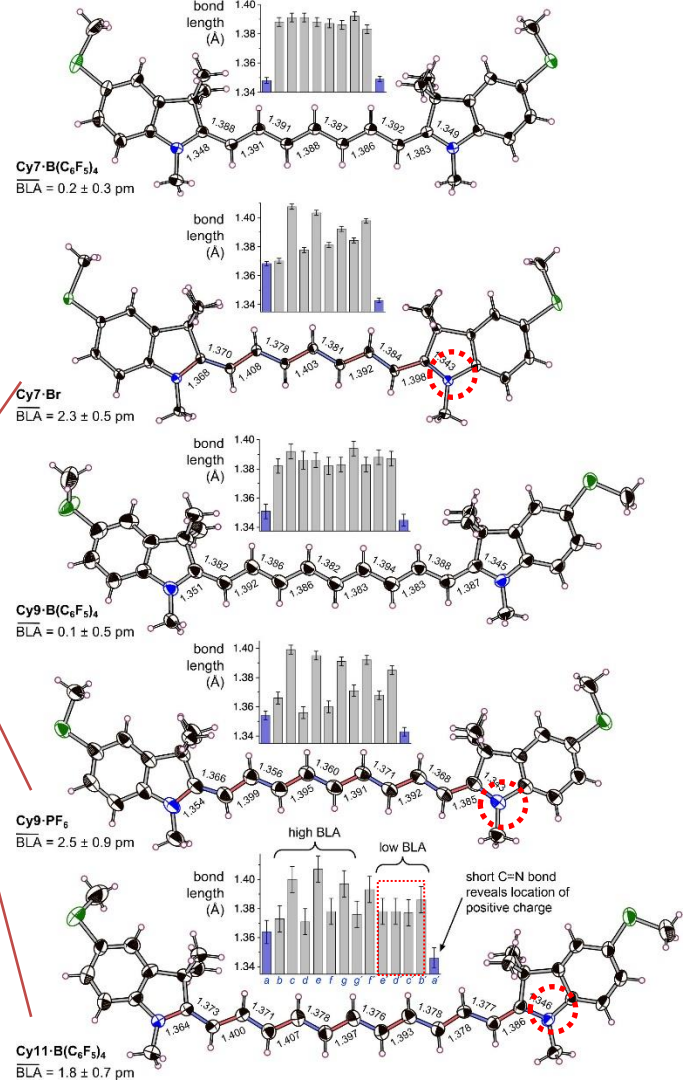


Crystallography

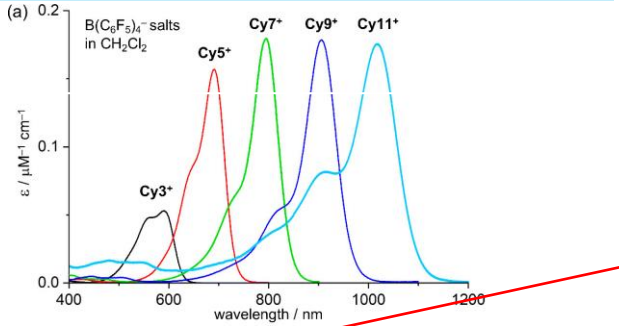
Table 4. Bond lengths and bond length alternation from this work for **Cy7**, **Cy9** and **Cy11**.

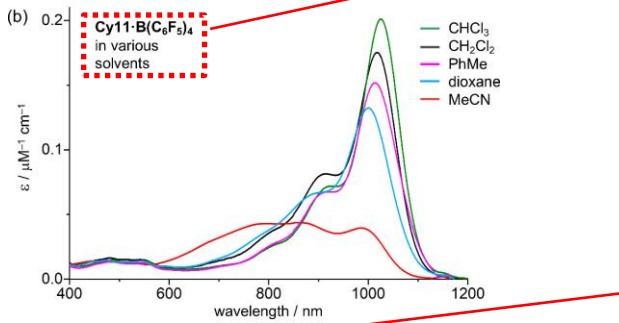
cyanine	Cy7	Cy7	Cy7	Cy9	Cy9	Cy11
X^-	$B(C_6F_5)_4^-$	PF_6^-	Br^-	$B(C_6F_5)_4^-$	PF_6^-	$B(C_6F_5)_4^-$
R factor	4.29%	6.88%	7.42%	6.52%	9.02%	6.80%
mean sd in bond lengths	±0.003	±0.011	±0.002	±0.006	±0.004	±0.009
a / Å	1.348(2)	1.363	1.3683(15)	1.351(5)	1.354(3)	1.364(8)
a′ / Å	1.349(2)	1.354	1.3428(16)	1.345(4)	1.343(3)	1.346(7)
a – *a′* / Å	–0.001	0.009	0.0255	0.006	0.011	0.018
b / Å	1.388(3)	1.396	1.3701(17)	1.382(5)	1.366(4)	1.373(9)
b′ / Å	1.383(3)	1.394	1.3978(16)	1.387(5)	1.385(3)	1.386(9)
b – *b′* / Å	0.005	0.002	–0.0277	–0.005	–0.019	–0.013
c / Å	1.391(3)	1.394	1.4076(17)	1.392(5)	1.399(3)	1.400(9)
c′ / Å	1.392(3)	1.379	1.3843(18)	1.388(5)	1.368(3)	1.377(9)
c – *c′* / Å	–0.001	0.015	0.0233	–0.004	0.031	0.023
d / Å	1.391(3)	1.375	1.3777(18)	1.386(6)	1.356(4)	1.371(9)
d′ / Å	1.386(3)	1.424	1.3922(18)	1.383(5)	1.392(3)	1.378(9)
d – *d′* / Å	0.005	–0.049	–0.0145	0.003	–0.036	–0.007
e / Å	1.388(3)	1.391	1.4033(17)	1.386(5)	1.395(3)	1.407(9)
e′ / Å	1.387(3)	1.368	1.3810(18)	1.394(5)	1.371(4)	1.378(9)
e – *e′* / Å	0.001	0.023	0.0223	–0.008	0.024	0.029
f / Å				1.382(6)	1.360(4)	1.378(9)
f′ / Å				1.383(5)	1.391(3)	1.393(9)
f – *f′* / Å				–0.001	–0.031	–0.015
g / Å						1.397(9)
g′ / Å						1.376(9)
g – *g′* / Å						0.021
mean BLA / Å	0.002	0.019	0.023	0.001	0.025	0.018
BLA sd / Å	±0.003	±0.019	±0.005	±0.005	±0.009	±0.007

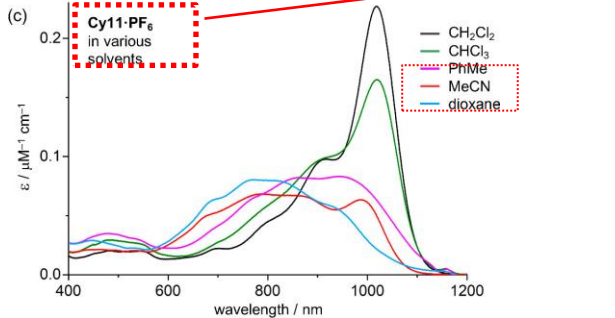
Significanct BLA

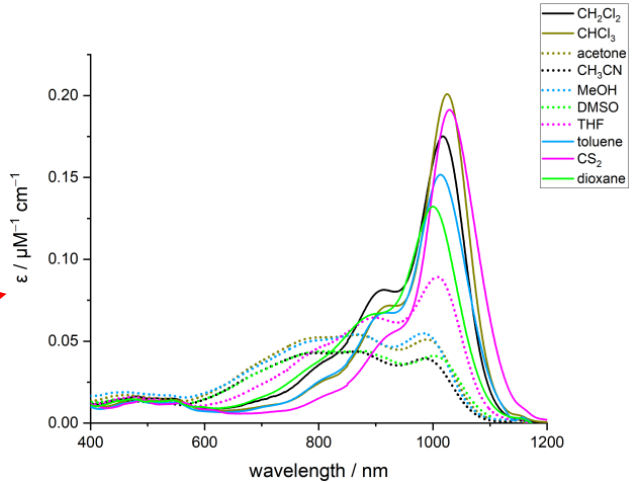


Absorption Spectra

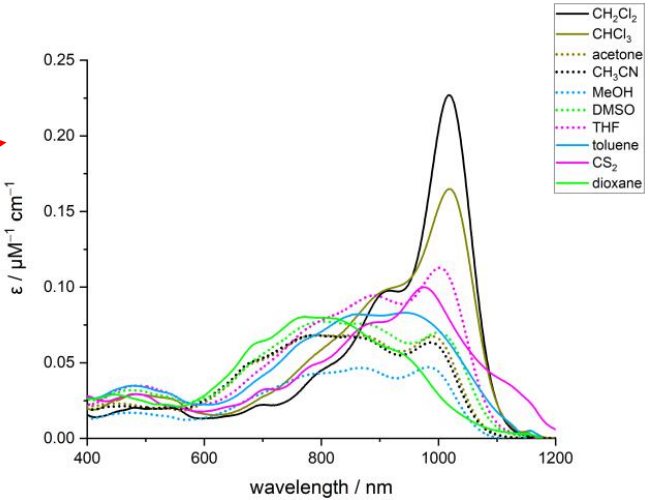






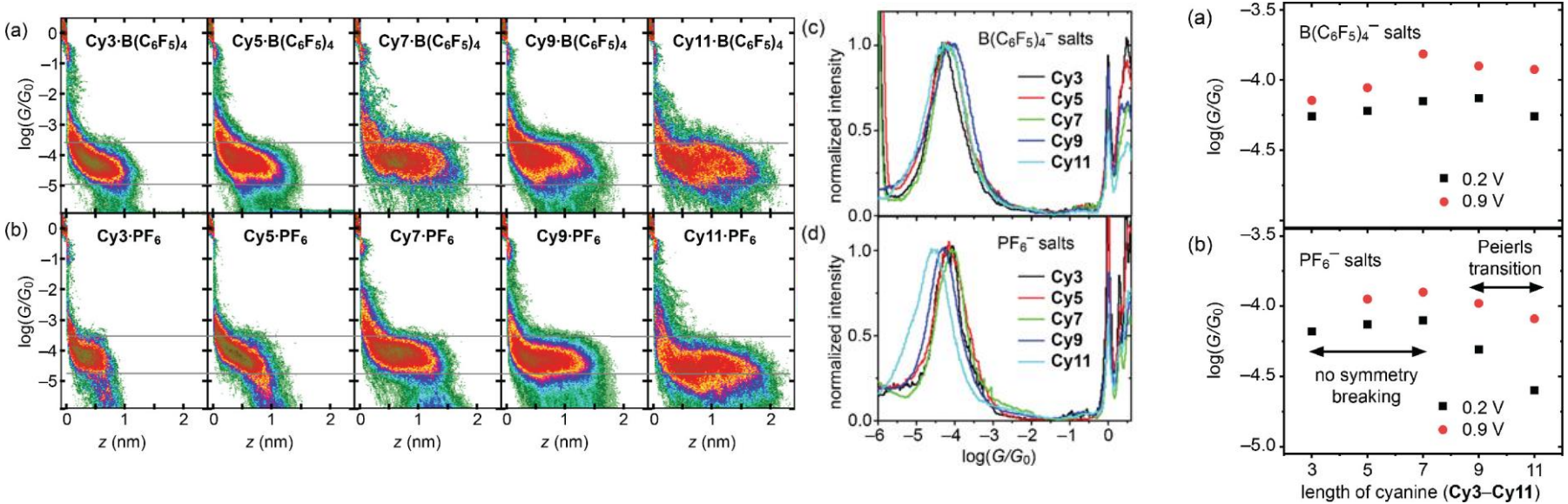


在其他极性溶剂如丙酮、甲醇和DMSO中具有类似的广谱。



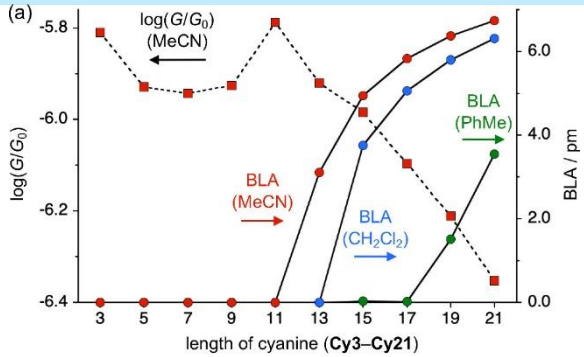
当溶剂变为二氯甲烷时，所有与极性溶剂有关的光谱变化立即恢复，证实广谱不是由于分解。

Single-Molecular Conductance

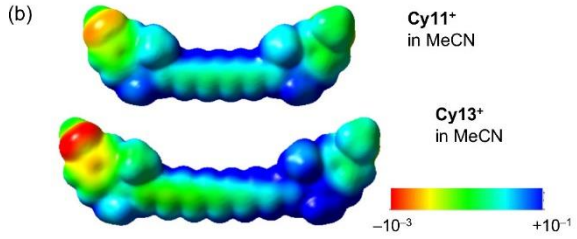


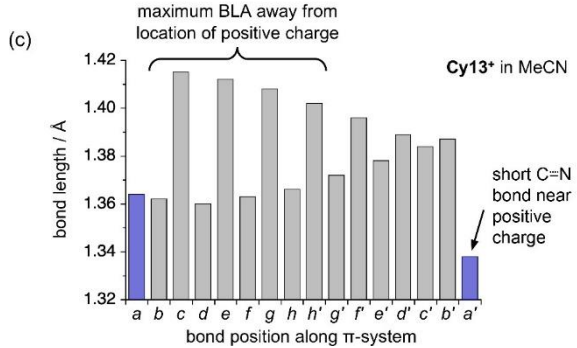
不清楚PF6 -相对于该离子对中的聚次甲基链的位置，无论处于什么位置，较小的反离子PF6 -都会使π-系统极化。除非它恰好在链两端之间的距离相等。

Computational Modeling



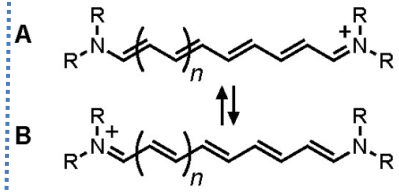
计算证实对称性破坏是由于环境极性引起的。





BHandHLYP functional (include 50% Hartree-Fock exchange)

应用变分法计算多电子体系波函数的方程。



cyanine	λ_{max} (nm)	E_{max} (eV)	f
$Cy3^+$	428	2.898	1.85
$Cy5^+$	490	2.529	2.43
$Cy7^+$	553	2.240	2.95
$Cy9^+$	616	2.014	3.44
$Cy11^+$	676	1.833	3.92
$Cy13^+$	735	1.687	4.37
$Cy15^+$	742	1.672	4.48
$Cy17^+$	736	1.685	4.56
$Cy19^+$	729	1.700	4.69
$Cy21^+$	722	1.718	4.85