Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting information

A joint experimental and theoretical study on the electro-optical properties of 1,6- and 1,7-fluorenyl disubstituted perylene diimide isomers

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SI-1. Synthetic procedure, NMR and MALDI-TOF

*N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide **PDI***

N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was obtained by a modified procedure from the literature [1S]. The condensation reaction of 3,4,9,10-perylenetetracarboxylic dianhydride (606 mg, 1.55 mmol) and 10-nonadecanamine (1.07 g, 3.78 mmol) was accomplished by conducting the imidization reaction in the presence of zinc acetate (214 mg, 1.16 mmol) in quinoline (5 ml) at 160 °C for 4 hours under nitrogen atmosphere. The resulting N, N'-bis-(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was isolated in 78% yield as a deep red solid after a silica gel column chromatography purification (hexane:$CHCl_3$=8:2 as eluent).

^{1}H-NMR ($CDCl_3$): δ 0.83 (t, 12H), 1.21 (m, 56H), 1.85 (m, 4H), 2.26 (m, 4H), 5.25 (m, 2H), 8.51 (br, 4H, pery-H), 8.59 (br, 4H, pery-H). IR (KBr, cm^{-1}): υ 2922, 2853, 1694, 1649, 1593, 1465, 1404, 1344, 1254, 1175

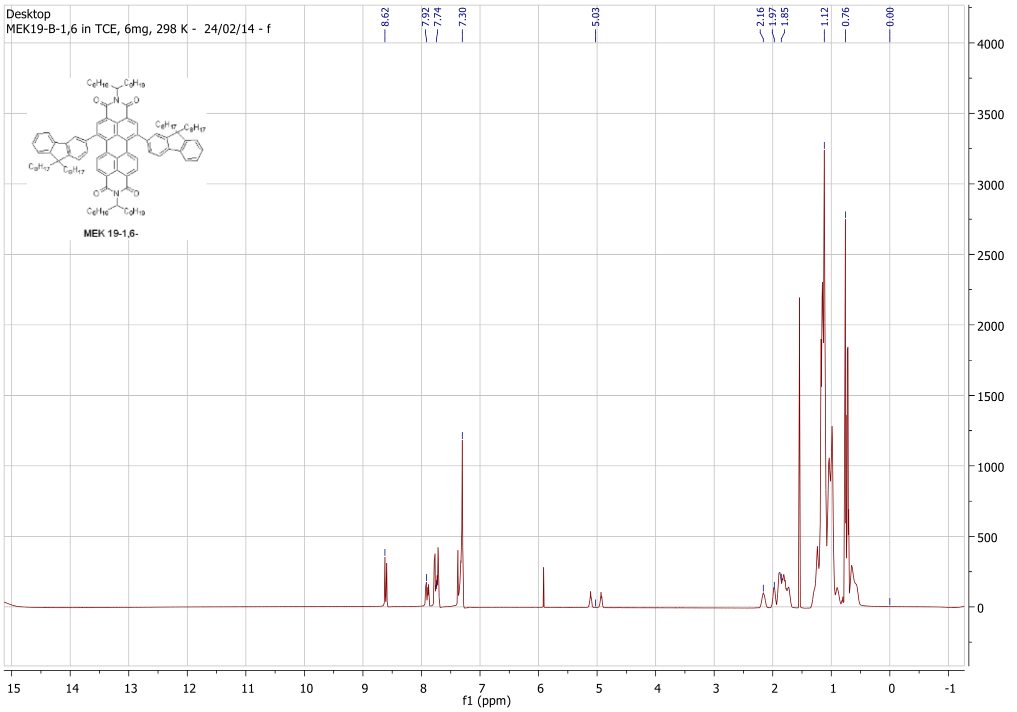
*Dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide **PDI-diBr** (mixture of 1,6- and 1,7- regioisomers)*

Dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide was obtained as described in literature [2S]. A mixture of N,N'-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic acid diimide (100 mg, 0.108 mmol), bromine (1184 mg, 7.4 mmol) in 2 ml CH_2Cl_2 was stirred at 60 °C in a closed vial for 4 hours. The reaction mixture was allowed to reach the room temperature and then, after removing the excess of bromine by air bubbling, the solvent was removed under vacuum. The crude product was purified by a silica gel column chromatography, using hexane:$CHCl_3$=6:4 as eluent. The first band was collected to afford dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide (as a mixture of 1,7-dibromo and 1,6-dibromo derivative 3:1) as a deep orange solid (108 mg, 92%). ^{1}H-NMR ($CDCl_3$): δ 0.85 (t, 12H), 1.25 (m, 56H), 1.85 (m, 4H), 2.25 (m, 4H), 5.20 (m, 2H), 8.70 (br, 2H, pery-H), 8.91 (br, 2H, pery-H), 9.52 (d, 2H, pery-H). IR (KBr, cm^{-1}): υ 2919, 2849, 1700, 1660, 1589, 1465, 1382, 1327, 1237

*1, 6- (**PDI-F1)** and 1,7-bis-2[9,9'-dioctylfluorenyl)]-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) (**PDI-F2**)*

A mixture of dibromo-N,N'-bis(10-nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide and 9,9-dioctylfluorene-2-boronic acid pinacol ester (2.04 equivalents) were dissolved in dry toluene (5 ml each 0.25 mmol of dibromo-N,N'-bis(nonadecyl)perylene-3,4,9,10-tetracarboxylic diimide) and 2M K_2CO_3 solution (1 ml each 4 ml of toluene). Catalytic amounts of Pd[PPh_3]$_4$ were added and the reaction mixture was stirred at 100 °C for 18 hours. Shortly after the addition of the catalyst, the colour of the mixture starts to change. At the end of the reaction time, the solution was cooled to room temperature, extracted with $CHCl_3$, washed with water, extracted and dried over $MgSO_4$ anh. concentrated to a smaller volume and dropped into methanol. The precipitate was filtered, and the two isomers were separated by column chromatography, using hexane/$CHCl_3$ 3:2 as eluent.

1,6-bis-2[9,9'-dioctylfluorenyl)]-N,N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) (***PDI-F1***) was obtained as a deep red solid in 26% yield. ^{1}H-NMR(TCE, 600MHz): δ =8.62 (2H, d, pery), 7.92 (2H, d, pery), 7.74 (6H, dd, pery, fluorene), 7.30 (10H, m, fluorene), 5.03 (2H, d, -CH-N), 2.16 (4H, d, -CH_2-), 1.85 (12H, m, -CH_2-), 1.12 (104H, m, -CH_2-), 0.76 (24H, -CH_3).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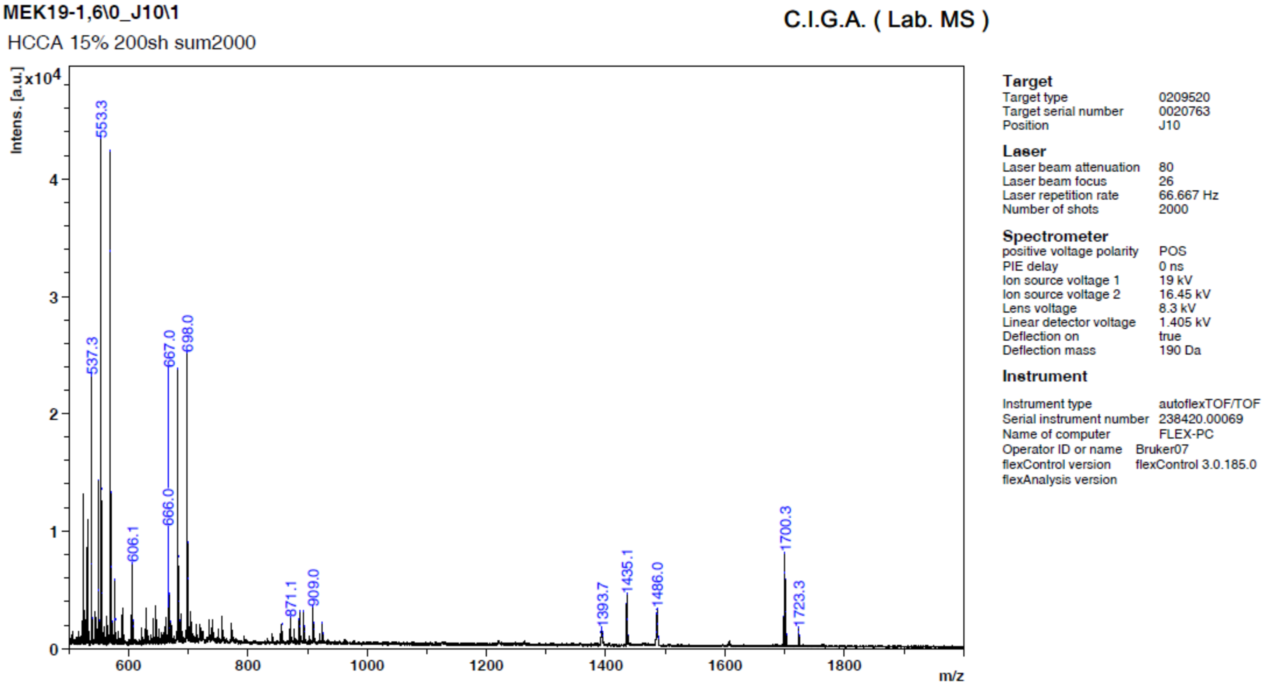
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C.I.G.A. (Lab. MS)

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Target serial number 0020763
Position J10

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Laser beam focus 26
Laser repetition rate 66.667 Hz
Number of shots 2000

Spectrometer
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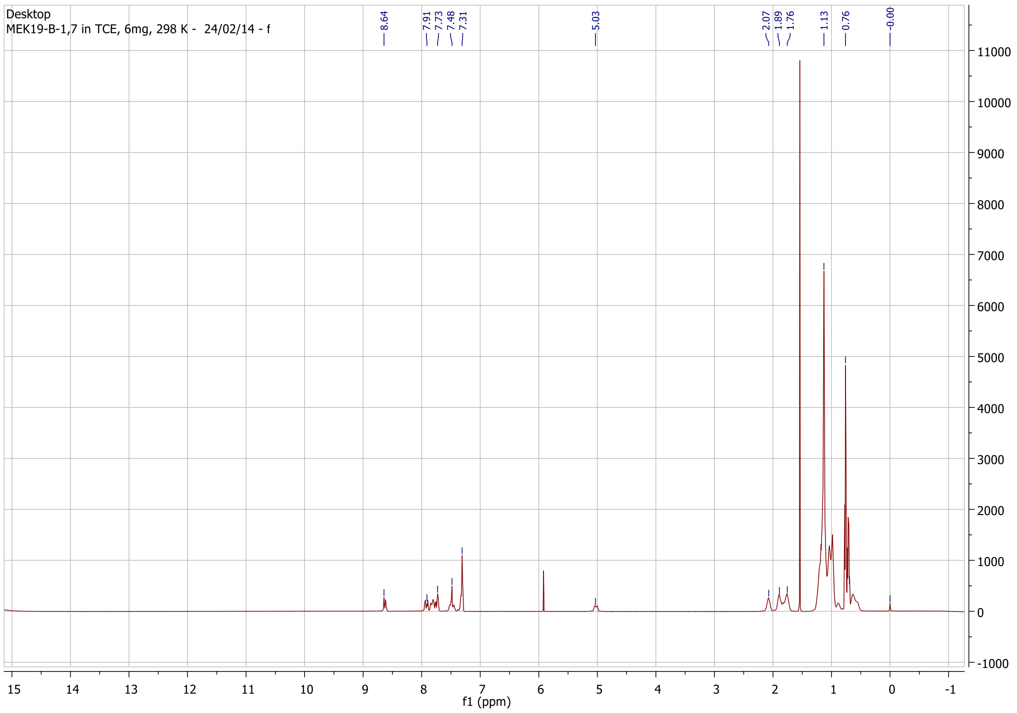
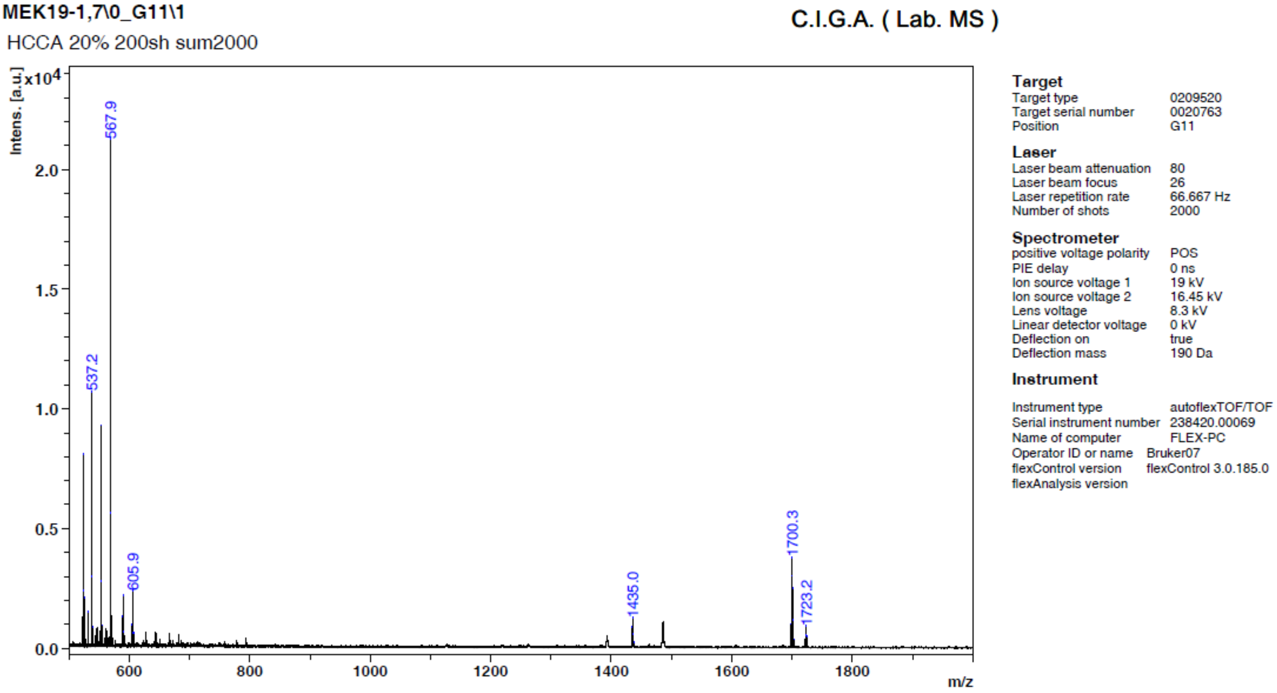
PIE delay 0 ns
Ion source voltage 1 19 kV
Ion source voltage 2 16.45 kV
Lens voltage 8.3 kV
Linear detector voltage 1.405 kV
Deflection on true
Deflection mass 190 Da

Instrument
Instrument type autoflexTOF/TOF
Serial instrument number 238420.00069
Name of computer FLEX-PC
Operator ID or name Bruker07
flexControl version flexControl 3.0.185.0
flexAnalysis version

1,7-bis-2[9,9'-dioctylfluorenyl)]-N, N'-bis-(10-nonadecyl)-perylene-3,4,9,10-bis(dicarboximide) (***PDI-F2***) was obtained as a dark violet solid in 62% yield. ^{1}H-NMR (TCE, 600MHz): δ =8.64 (2H, d, pery), 7.91 (2H, d, pery), 7.73 (6H, dd, pery, fluorene), 7.31 (10H, m, fluorene), 5.03 (2H, d, -CH-N), 2.07 (4H, d, $-CH_2-$), 1.89 (12H, m, $-CH_2-$), 1.13 (104H, m, $-CH_2-$), 0.76 (24H, $-CH_3$).





MEK19-1,7\0_G11\1

HCCA 20% 200sh sum2000

C.I.G.A. (Lab. MS)

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Laser repetition rate	66.667 Hz
Number of shots	2000

Spectrometer

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Ion source voltage 2	16.45 kV
Lens voltage	8.3 kV
Linear detector voltage	0 kV
Deflection on	true
Deflection mass	190 Da

Instrument

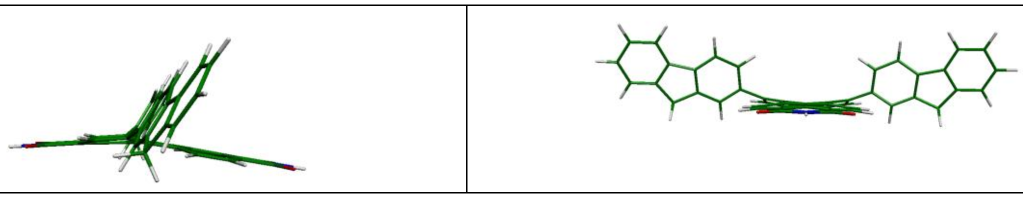
Instrument type	autoflexTOF/TOF
Serial instrument number	238420.00069
Name of computer	FLEX-PC
Operator ID or name	Bruker07
flexControl version	flexControl 3.0.185.0
flexAnalysis version	

SI-2. Solvent dielectric constants (ε) and the refractive indexes (n) and determination of the orientation polarizability (Δf)

$\Delta f = f(\varepsilon) - f(n^2) = (\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$

Solvent	ε	n	ε-1	2ε+1	n^2-1	2n^2+1	Δf
Cyclohexane	2.02	1.4262	0.202380952	1.03404644	5.06809288	0.204030681	-0.001649728
Diethylether	4.33	1.3524	0.344720497	0.82898576	4.65797152	0.17797141	0.166749087
THF	7.58	1.4072	0.407178218	0.98021184	4.96042368	0.197606475	0.209571742
Ethylacetate	6.02	1.3724	0.384969325	0.88348176	4.76696352	0.185334282	0.199635043
Dichloromethane	8.93	1.4241	0.420466596	1.02806081	5.05612162	0.203329921	0.217136675
DMF	36.7	1.4305	0.47983871	1.04633025	5.0926605	0.205458473	0.274380237
Chloroform	4.81	1.4458	0.358757062	1.09033764	5.18067528	0.210462455	0.148294607

BIS / C_{2v}
E = –1330.170524 hartree



PD1-F1(I)/ C_s
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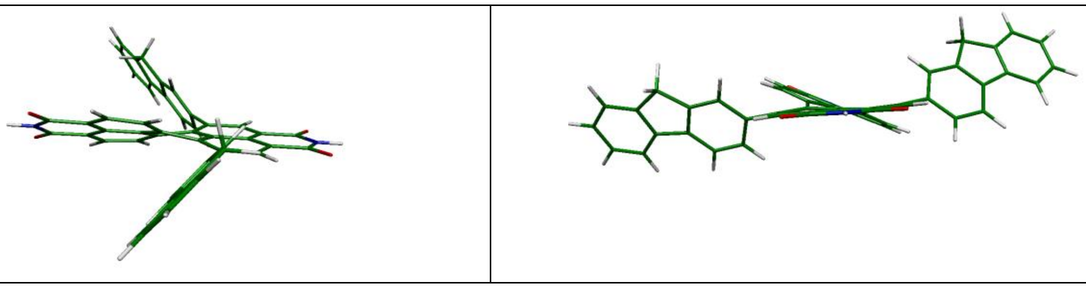
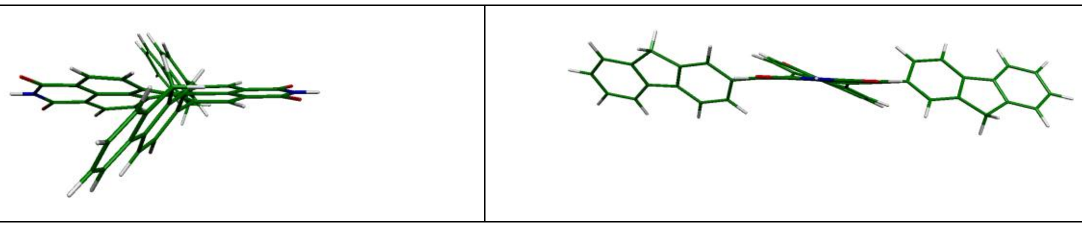


PD1-F1(II)/ C_1
E = –2329.896500 hartree



PD1-F1(III)/ C_1
E = –2329.896380 hartree

Fig. 1S. The side and frontal views on the B3LYP optimal geometries of the calculated model molecules in the electronic ground state. Propyl and iso-heptyl groups replace the C_8H_{17} and $CH(C_9H_{19})$ groups for clarity. Symmetry point group is indicated after slash symbols.

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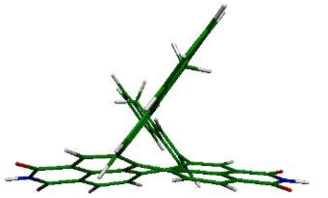
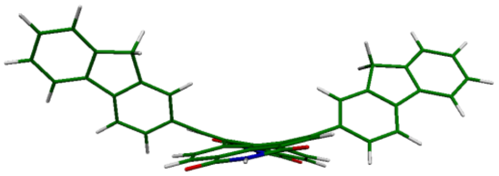
<tr><td></td><td></td></tr>
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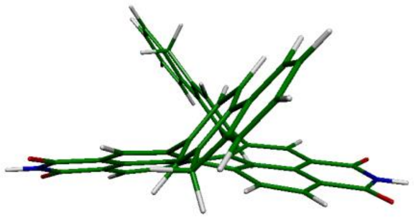
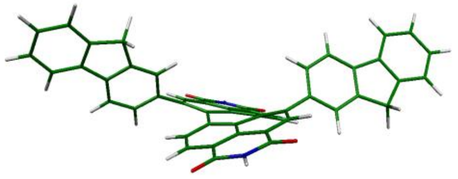
<tr><td></td><td></td></tr>
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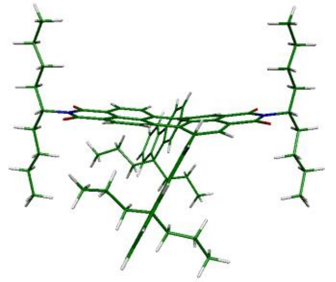
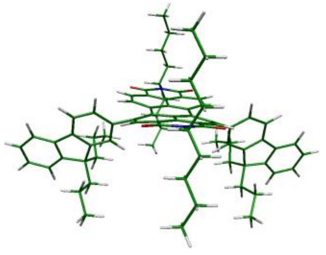
<tr><td></td><td></td></tr>
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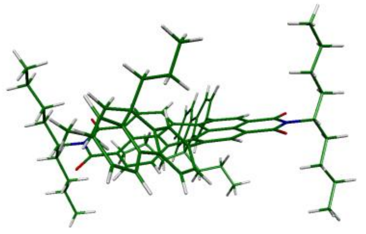
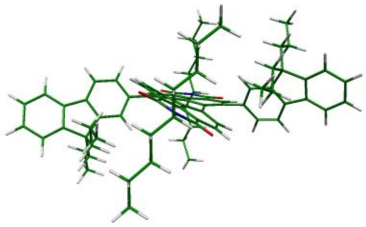
<tr><td></td><td></td></tr>
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Fig. 1S (continued). The side and frontal views on the B3LYP optimal geometries of the calculated model molecules in the electronic ground state. Propyl and iso-heptyl groups replace the C_8H_{17} and $CH(C_9H_{19})$ groups for clarity. Symmetry point group is indicated after slash symbols.

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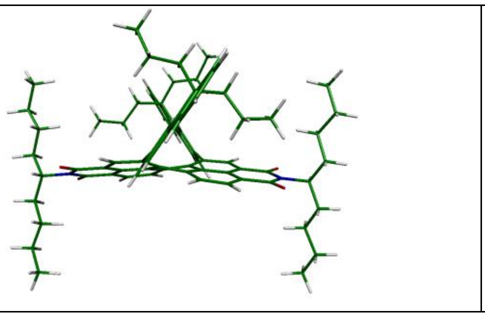
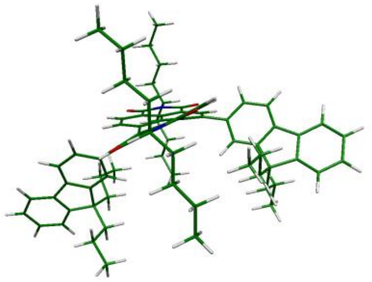
<tr><td></td><td></td></tr>
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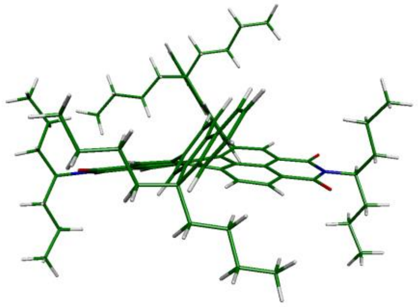
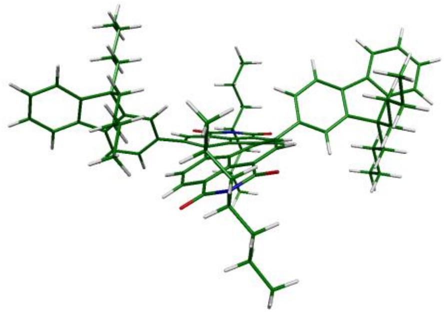
<tr><td></td><td></td></tr>
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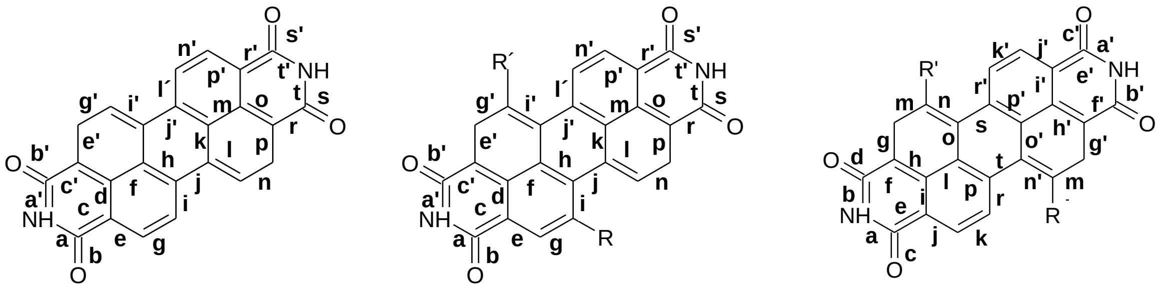
Fig. 1S (continued). The side and frontal views on the B3LYP optimal geometries of the calculated model molecules in the electronic ground state. Propyl and iso-heptyl groups replace the C_8H_{17} and $CH(C_9H_{19})$ groups for clarity. Symmetry point group is indicated after slash symbols.



BIS **PD1-F1** **PD1-F2**

Fig. 2S. The bond notations and the definition of dihedral angles for studied molecules. For **BIS** and **PD1-F1** are ϑ_1 (i´–l´), ϑ_2 (i–l), ϑ_3 (i´–i) and ϑ_4 (l-l´) and for **PD1-F2** are ϑ_1 (r– r´), ϑ_2 (n´–r´), ϑ_3 (l–l´) and ϑ_4 (i-i´). The dihedral angles Ω/Ω^* represent the torsion between the central bonds n,n´or i,i´ with respect to the fluorenyl central plane.

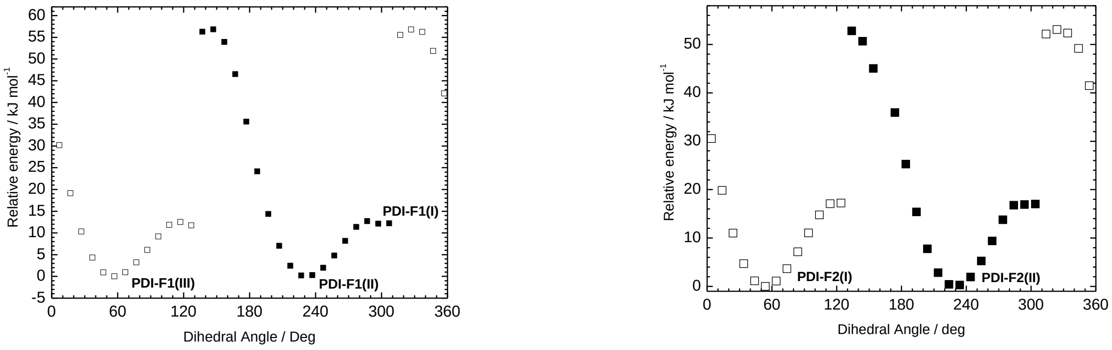
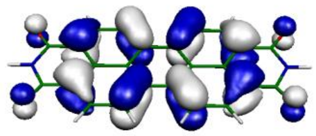
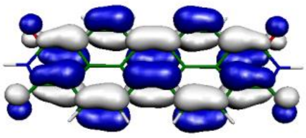
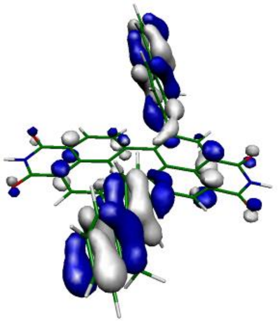
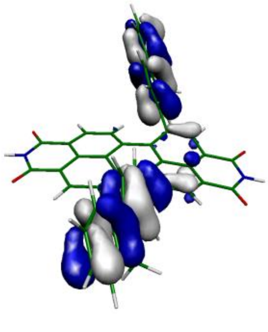


Fig. 3S. The torsional dependence of relative electronic B3LYP energy on the dihedral angle Ω_1 for the calculated **PDI-F1** (left) and **PDI-F2** (right) molecules. Relative energies are calculated with respect to the global minima, i.e. **PDI-F1(II)** and **PDI-F2(I)**.

BIS / C$_{2v}$

	
HOMO / a2	LUMO / b1

PDI-F1(I) / C$_s$

	
HOMO–2 / a´´	HOMO–1 / a´

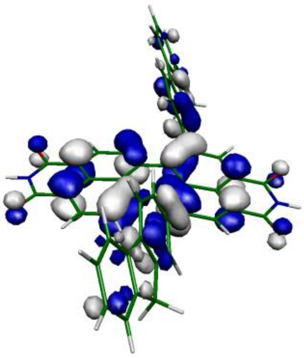
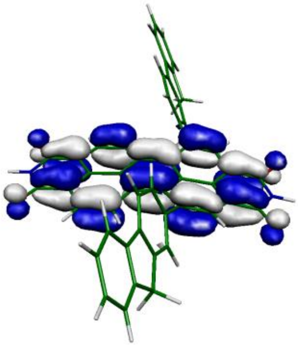
	
HOMO / a´´	LUMO / a´´

Fig. 4S. The selected B3LYP frontier orbitals for the symmetric geometries of **BIS**, **PID-F1(I)** and **PDI-F2(II)**. The orbital symmetry is indicated after slash symbol. The depicted iso-contour value is 0.03 au.

PDI-F2(I) / C$_2$

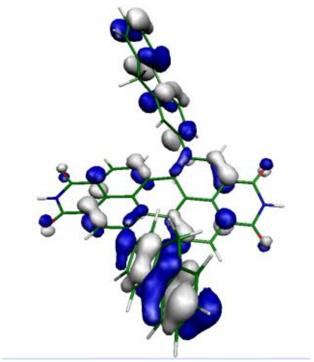
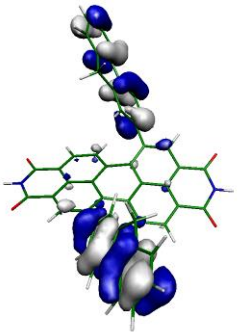
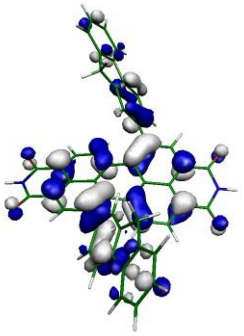
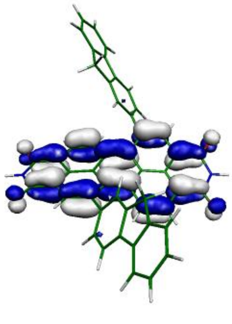
	
HOMO–2 / a	HOMO–1 / b
	
HOMO / a	LUMO / b

Fig. 4S (continued). The selected B3LYP frontier orbitals for the symmetric geometries of **BIS**, **PID-F1(I)** and **PDI-F2(II)**. The orbital symmetry is indicated after slash symbol. The depicted iso-contour value is 0.03 au.

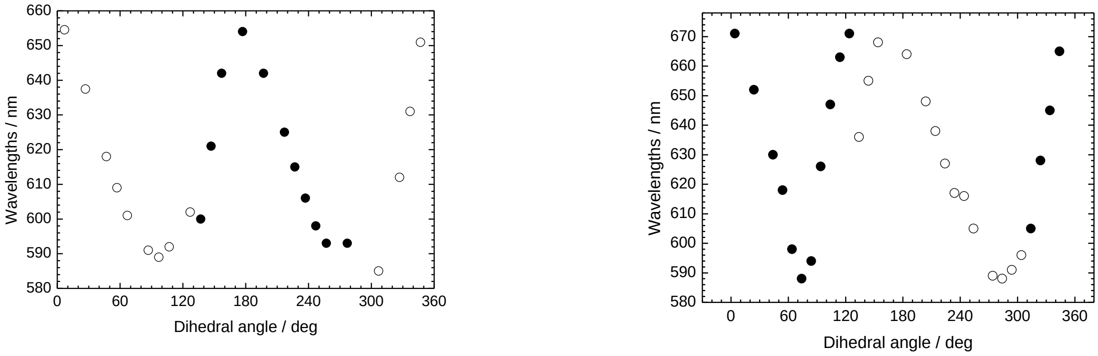


Fig. 5S. The torsional dependence of TD-B3LYP vertical excitation energies on the dihedral angle *Ω* for the calculated **PDI-F1** (left) and **PDI-F2** (right) molecules.

Table 1S. The selected dihedral angles for the optimal (TD-)B3LYP geometries of the electronic ground (S_0) and lowest energy excited (S_1) states. The data for S_1 are written in italic.

	ϑ_1 / deg	ϑ_2 / deg	ϑ_3 / deg	ϑ_4 / deg	Ω/ deg	Ω⍰ / deg
BIS	180 *180*	180 *180*	0 *0*	0 *0*	- -	- -
PDI-F1(I)	348 *348*	12 *12*	0 *0*	0 *0*	233 *219*	127 *141*
PDI-F1(II)	21 *20*	21 *20*	328 *330*	324 *325*	232 *218*	57 *47*
PDI-F1(III)	21 *19*	20 *19*	328 *330*	324 *325*	231 *221*	237 *221*
PDI-F2(I)	20 *19*	20 *19*	327 *328*	327 *328*	54 *41*	54 *41*
PDI-F2(II)	20 *19*	20 *19*	327 *328*	327 *328*	53 *41*	230 *217*
PDI-F1(I)-alkyl	348 *349*	12 *11*	0 *0*	0 *0*	231 *221*	129 *141*
PDI-F1(II)-alkyl	340 *342*	340 *342*	29 *26*	35 *34*	298 *312*	301 *302*
PDI-F2(I)-alkyl	19 *19*	19 *19*	329 *328*	329 *328*	57 *39*	57 *39*
PDI-F2(II)-alkyl	19 *19*	19 *18*	329 *329*	329 *329*	57 *44*	229 *215*

Table 2S. The (TD-)B3LYP bond lengths of symmetric **BIS**, **PDI-F1** and **PDI-F2** compounds for the electronic ground state (S_0) and lowest excited state (S_1) geometries. The sum of bond differences (ΣΔd) and the sum of absolute bond (Σ /Δd/) differences are calculated between the geometries of S_0 and S_1 states. All bond lengths are in angstroms.

Bond	**BIS**	**BIS**		**PDI-F2(I)**	**PDI-F2(I)**		**PDI-F1(I)**	**PDI-F1(I)**
	S_0	S_1		S_0	S_1		S_0	S_1
a	1.393	1.392		1.394	1.394		1.392	1.394
b	1.215	1.219		1.393	1.394		1.216	1.220
c	1.488	1.481		1.216	1.220		1.487	1.478
d	1.422	1.421		1.215	1.220		1.421	1.417
e	1.386	1.403		1.486	1.479		1.384	1.394
f	1.433	1.433		1.488	1.479		1.438	1.434
g	1.401	1.385		1.381	1.392		1.399	1.448
h	1.434	1.432		1.420	1.422		1.436	1.435
I	1.398	1.426		1.421	1.418		1.401	1.425
j	1.473	1.446		1.386	1.401		1.477	1.448
k	1.434	1.432		1.401	1.387		1.445	1.435
l	1.398	1.426		1.430	1.434		1.421	1.425
m	1.433	1.433		1.415	1.403		1.432	1.438
n	1.401	1.385		1.416	1.444		1.412	1.389
o	1.422	1.421		1.437	1.432		1.418	1.421
p	1.386	1.403		1.436	1.436		1.379	1.398
r	1.488	1.481		1.400	1.422		1.487	1.480
s	1.215	1.219		1.476	1.449		1.216	1.220
t	1.393	1.392		1.476	1.449		1.392	1.393
ΣΔd		–0.017			0.012			–0.039
Σ /Δd/		0.179			0.196			0.213

Table 3S. The lowest three TD-(CAM-)B3LYP//(TD-)B3LYP vertical optical transitions for the studied model molecules. The oscillator strengths are written after slash symbol. The values in parentheses stand for percentages of the excitation contributions in individual transitions.

Molecule	TD-B3LYP			TD-CAM-B3LYP	
	($S_0 \rightarrow S_{1/2/3}$)		($S_1 \rightarrow S_0$)	($S_0 \rightarrow S_{1/2/3}$)	($S_1 \rightarrow S_0$)
BIS	509 nm / 0.614	H → L (0.99)	561 nm / 0.594	453 nm / 0.736	605 nm / 0.384
	394 nm / 0.000	H–1 → L (0.95)		328 nm / 0.000	
	394 nm / 0.000	H → L (0.95)		309 nm / 0.063	
PDI-F1(I)	602 nm / 0.215	H → L (0.95)	725 nm / 0.204	494 nm / 0.472	600 nm / 0.378
	555 nm / 0.151	H–1 → L (0.99)		395 nm / 0.294	
	475 nm / 0.246	H–2 → L (0.94)		349 nm / 0.133	
PDI-F1(II)	609 nm / 0.168	H → L (0.96)	730 nm / 0.152	493 nm / 0.398	591 nm / 0.315
	561 nm / 0,153	H–1 → L (0.99)		396 nm / 0.291	
	470 nm / 0.244	H–2 → L (0.96)		345 nm / 0.162	
PDI-F1(III)	606 nm / 0.176	H → L (0.96)	726 nm / 0.158	490 nm / 0.418	590 nm / 0.329
	557 nm / 0.139	H–1 → L (0.99)		393 nm / 0.273	
	468 nm / 0.253	H–2 → L (0.95)		344 nm / 0.155	
PDI-F2(I)	618 nm / 0.260	H → L (0.96)	741 nm / 0.272	499 nm / 0.446	605 nm / 0.384
	543 nm / 0.022	H–1 → L (0.99)		386 nm / 0.042	
	475 nm / 0.290	H–2 → L (0.95)		356 nm / 0.415	
PDI-F2(II)	621 nm / 0.276	H → L (0.97)	742 nm / 0.289	501 nm / 0.461	603 nm / 0.407
	545 nm / 0.018	H–1 → L (0.99)		387 nm / 0.037	
	472 nm / 0.290	H–2 → L (0.95)		355 nm / 0.426	
PDI-F1(I)-alkyl	608 nm / 0.275	H → L (0.95)	727 nm / 0.253	502 nm / 0.563	604 nm / 0.466
	557 nm / 0.157	H–1 → L (0.99)		398 nm / 0.306	
	477 nm /0.276	H–2 → L (0.94)		349 nm / 0.153	
PDI-F1(II)-alkyl	608 nm / 0.207	H → L (0.96)	719 nm / 0.190	494 nm / 0.501	589 nm / 0.401
	562 nm / 0.114	H–1 → L (0.99)		392 nm / 0.231	
	483 nm / 0.290	H–2 → L (0.95)		350 nm / 0.159	
PDI-F2(I)-alkyl	621 nm / 0.271	H → L (0.96)	762 nm / 0.281	503 nm / 0.512	621 nm / 0.415
	548 nm / 0.017	H–1 → L (0.99)		386 nm / 0.035	
	483 nm / 0.332	H–2 → L (0.95)		359 nm / 0.407	
PDI-F2(II)-alkyl	625 nm / 0.308	H → L (0.97)	753 nm / 0.318	505 nm / 0.542	613 nm / 0.469
	550 nm / 0.015	H–1 → L (0.99)		388 nm / 0.031	
	480 nm / 0.330	H–2 → L (0.96)		358 nm / 0.429	

Table 4S. The lowest TD-(CAM-) B3LYP(SMD)//(TD-)B3LYP vertical optical transitions for the largest studied model molecules. The oscillator strengths are written after slash symbol.

Molecule	Cyclohexane		Chloroform		Cyclohexane		Chloroform	
	$(S_0 \rightarrow S_1)$	$(S_1 \rightarrow S_0)$	$(S_0 \rightarrow S_1)$	$(S_1 \rightarrow S_0)$	$(S_0 \rightarrow S_1)$	$(S_1 \rightarrow S_0)$	$(S_0 \rightarrow S_1)$	$(S_1 \rightarrow S_0)$
PDI-F1(I)-alkyl	624 nm / 0.347	761 nm/ 0.327	628 nm /0.351	768 nm/ 0.330	517 nm /0.683	631 nm/ 0.576	519 nm / 0.694	635 nm/ 0.586
PDI-F1(II)-alkyl	624 nm / 0.293	745 nm/ 0.262	627 nm /0.301	749 nm/ 0.269	509 nm / 0.637	611 nm/ 0.524	511 nm / 0.649	614 nm/ 0.536
PDI-F2(I)-alkyl	639 nm/ 0.356	794 nm /0.359	643 nm / 0.362	798 nm / 0.365	519 nm / 0.643.	646 nm / 0.523	521 nm / 0.654	648 nm / 0.533
PDI-F2(II)-alkyl	645 nm / 0.391	785 nm / 0.395	648 nm / 0.396	786 nm / 0.395	522 nm / 0.667	639 nm / 0.575	524 nm / 0.678	641 nm / 0.585

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