Electronic Supporting Information for

"Polarized molecular wires for efficient photo-generation of free electric charge carriers"

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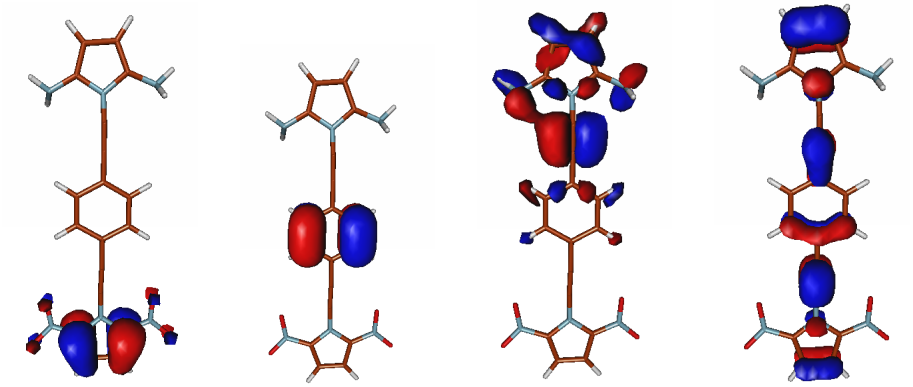
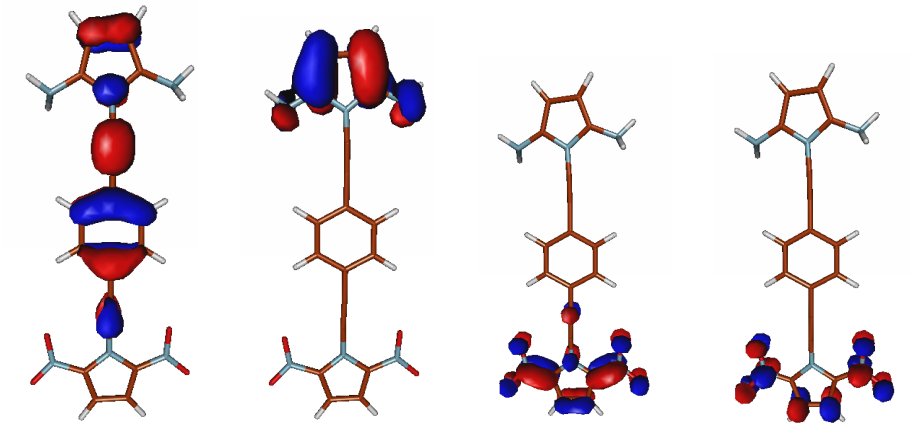
S1 Active space orbitals of the PMWs

S1.1 Pyrro-I

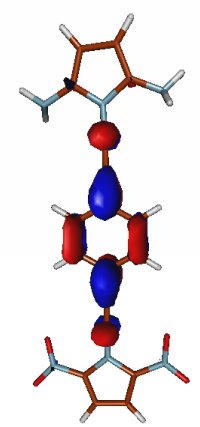


(a) H-5 orbital of **pyrro-I** (b) H-4 orbital of **pyrro-I** (c) H-3 orbital of **pyrro-I** (d) H-2 orbital of **pyrro-I**

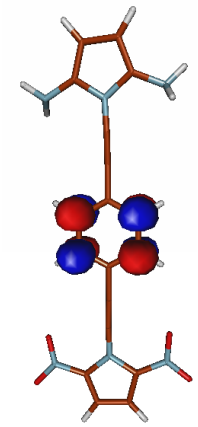


(e) H-1 orbital of **pyrro-I** (f) HOMO orbital of **pyrro-I** (g) LUMO orbital of **pyrro-I** (h) L+1 orbital of **pyrro-I**

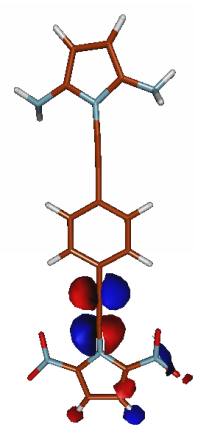
Figure S1: Active space orbitals of **pyrro-I**, used in the ODM2/MRCI-SD calculations.



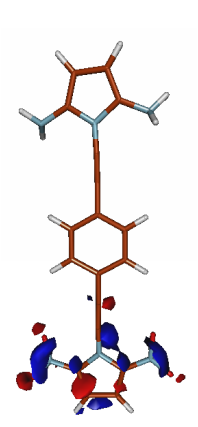
(i) L+2 orbital of **pyrro-I**



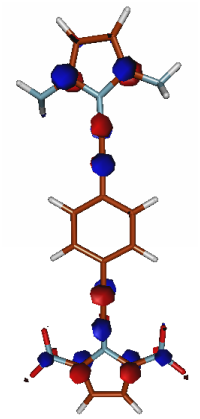
(j) L+3 orbital of **pyrro-I**



(k) L+4 orbital of **pyrro-I**



(l) L+5 orbital of **pyrro-I**



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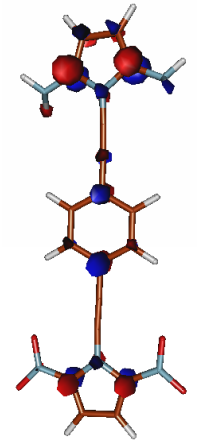
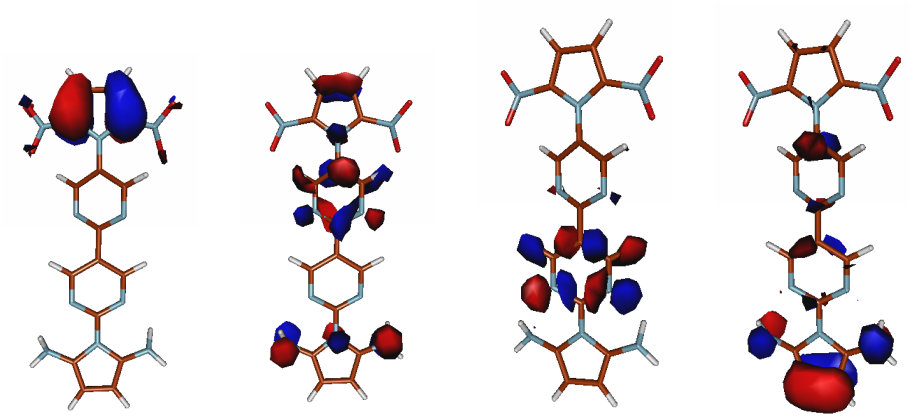
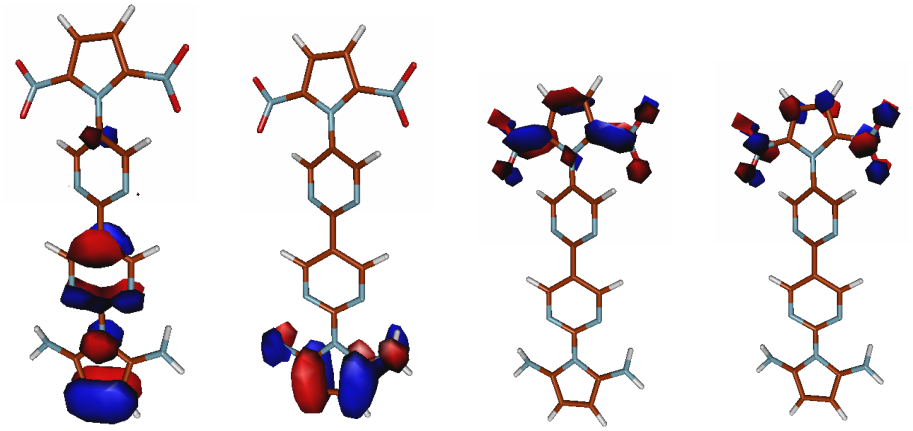


(n) L+7 orbital of **pyrro-I**

S1.2 Pyrro-II

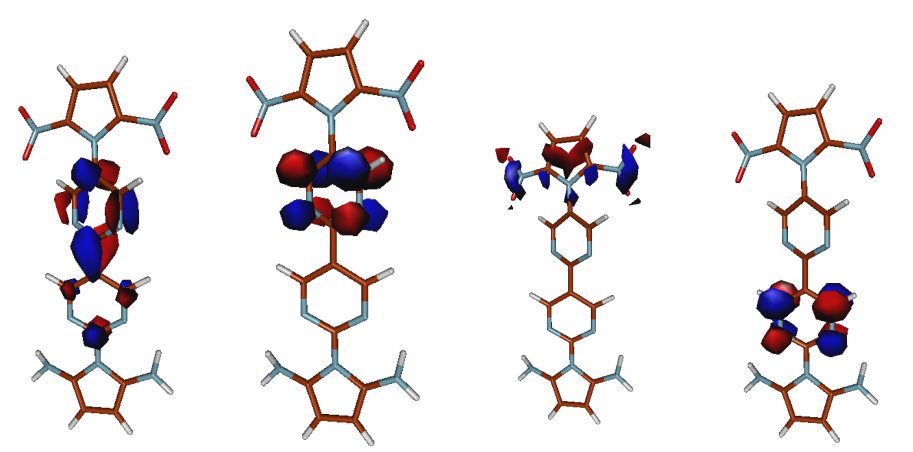


(a) H-5 orbital of **pyrro-II** (b) H-4 orbital of **pyrro-II** (c) H-3 orbital of **pyrro-II** (d) H-2 orbital of **pyrro-II**



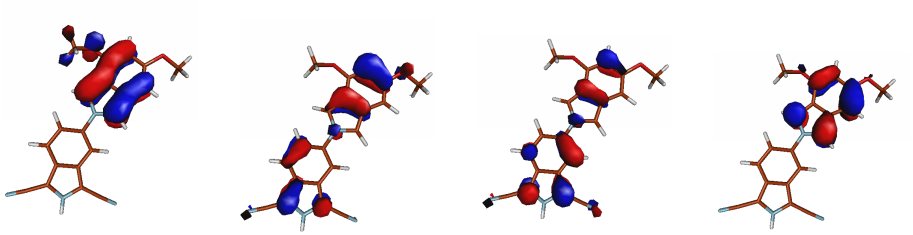
(e) H-1 orbital of **pyrro-II** (f) HOMO orbital of **pyrro-II** (g) LUMO orbital of **pyrro-II** (h) L+1 orbital of **pyrro-II**

Figure S2: Active space orbitals of **pyrro-II**, used in the ODM2/MRCI-SD calculations.

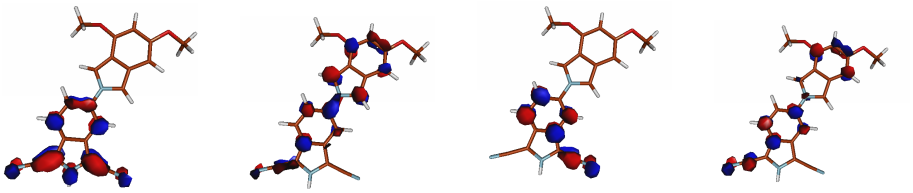


(i) L+2 orbital of **pyrro-II** (j) L+3 orbital of **pyrro-II** (k) L+4 orbital of **pyrro-II** (l) L+5 orbital of **pyrro-II**

S1.3 Isoindole-I



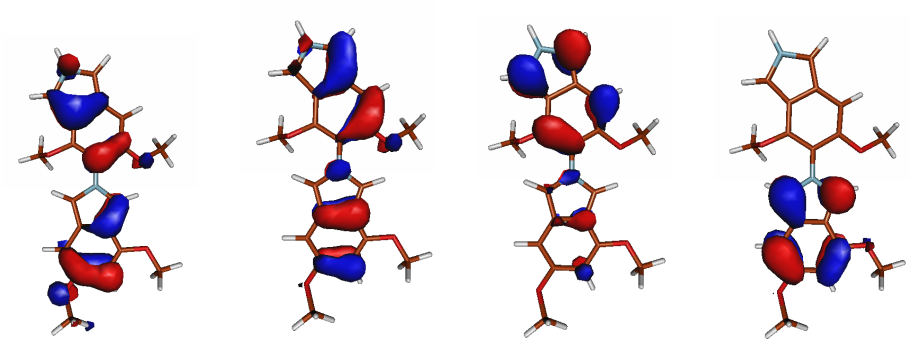
(a) H-3 orbital of **isoindole-I** (b) H-2 orbital of **isoindole-I** (c) H-1 orbital of **isoindole-I** (d) HOMO orbital of **isoindole-I**



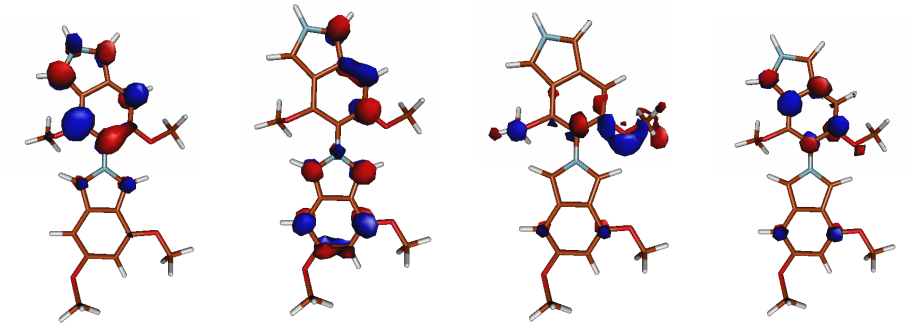
(e) LUMO orbital of **isoindole-I** (f) L+1 orbital of **isoindole-I** (g) L+2 orbital of **isoindole-I** (h) L+3 orbital of **isoindole-I**

Figure S3: Active space orbitals of **Isoindole-I**, used in the ODM2/MRCI-SD calculations.

S1.4 Isoindole-II



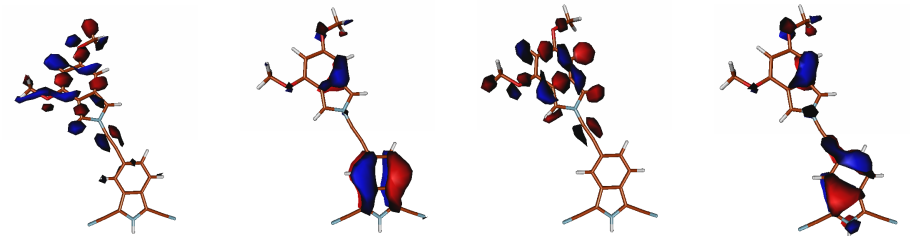
(a) H-3 orbital of **isoindole-II** (b) H-2 orbital of **isoindole-II** (c) H-1 orbital of **isoindole-II** (d) HOMO orbital of **isoindole-II**



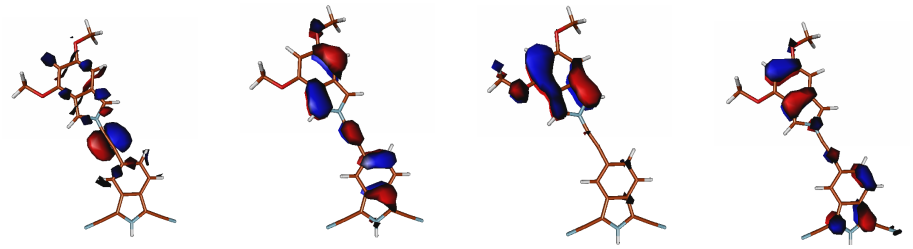
(e) LUMO orbital of **isoindole-II** (f) L+1 orbital of **isoindole-II** (g) L+2 orbital of **isoindole-II** (h) L+3 orbital of **Isoindole-II**

Figure S4: Active space orbitals of **Isoindole-II**, used in the ODM2/MRCI-SD calculations.

S1.5 Isoindole-I-CC

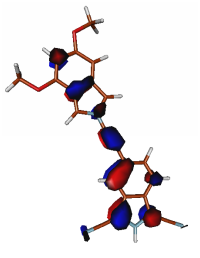
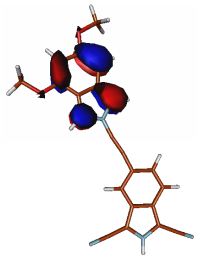
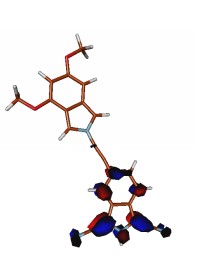
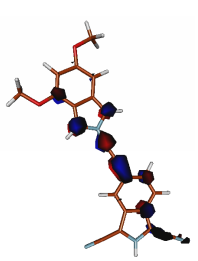


(a) H-9 orbital of **Isoindole-I-CC** (b) H-8 orbital of **Isoindole-I-CC** (c) H-7 orbital of **Isoindole-I-CC** (d) H-6 orbital of **Isoindole-I-CC**

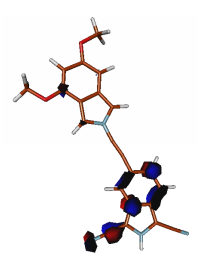
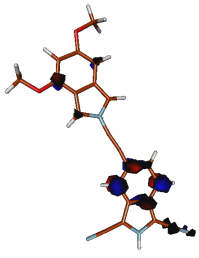
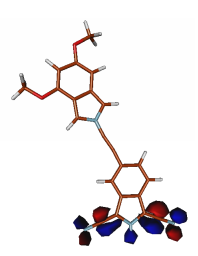
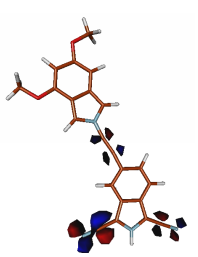


(e) H-5 orbital of **Isoindole-I-CC** (f) H-4 orbital of **Isoindole-I-CC** (g) H-3 orbital of **Isoindole-I-CC** (h) H-2 orbital of **Isoindole-I-CC**

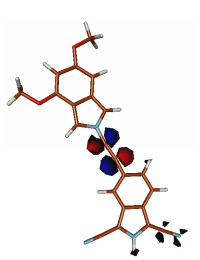
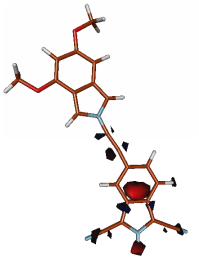
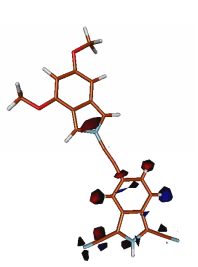
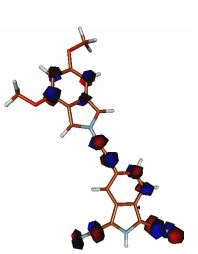
Figure S5: Active space orbitals of **Isoindole-I-CC**, used in the ODM2/MRCI-SD calculations.

(i) H-1 orbital of **Isoindole-I-CC** (j) HOMO orbital of **Isoindole-I-CC** (k) LUMO orbital of **Isoindole-I-CC** (l) L+1 orbital of **Isoindole-I-CC**

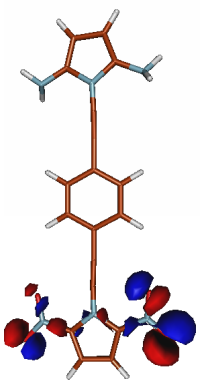
(m) L+2 orbital of **Isoindole-I-CC** (n) L+3 orbital of **Isoindole-I-CC** (o) L+4 orbital of **Isoindole-I-CC** (p) L+5 orbital of **Isoindole-I-CC**

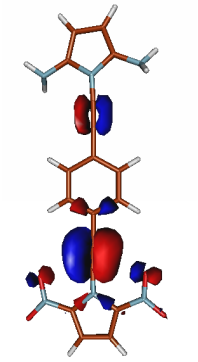
(q) L+6 orbital of **Isoindole-I-CC** (r) L+7 orbital of **Isoindole-I-CC** (s) L+8 orbital of **Isoindole-I-CC** (t) L+9 orbital of **Isoindole-I-CC**

S2 ADC2 orbitals of the PMWs

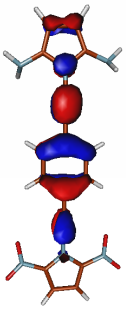
S2.1 Pyrro-I



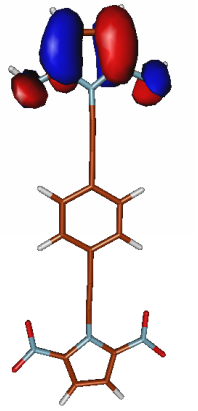
(a) H-13 orbital of **Pyrro-I**



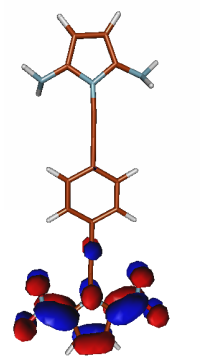
(b) H-8 orbital of **Pyrro-I**



(c) H-1 orbital of **Pyrro-I**



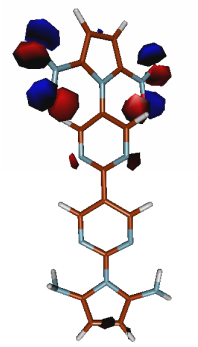
(d) HOMO orbital of **Pyrro-I**



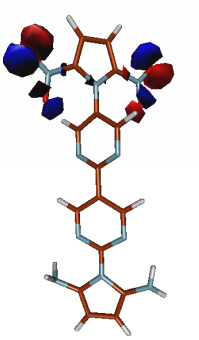
(e) LUMO orbital of **Pyrro-I**

Figure S6: Relevant orbitals of **Pyrro-I**, computed at the ADC(2) level of theory.

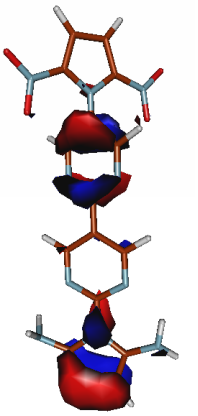
S2.2 Pyrro-II



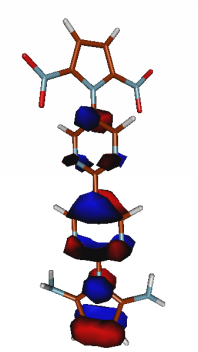
(a) H-19 orbital of **Pyrro-II**



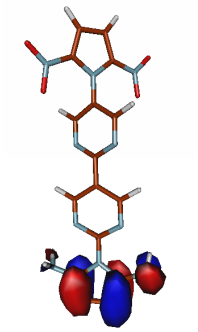
(b) H-17 orbital of **Pyrro-II**



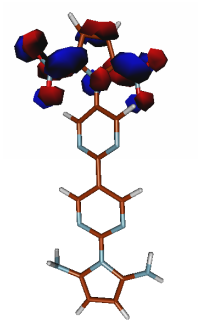
(c) H-2 orbital of **Pyrro-II**



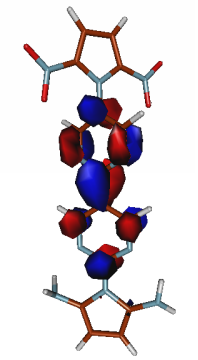
(d) H-1 orbital of **Pyrro-II**



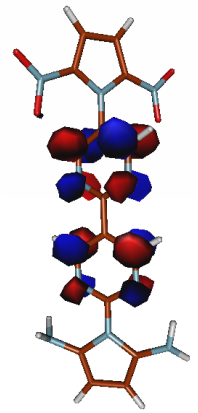
(e) HOMO orbital of **Pyrro-II**



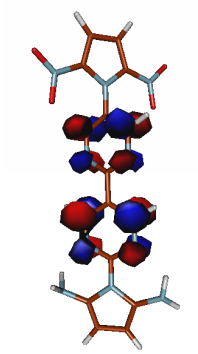
(f) LUMO orbital of **Pyrro-II**



(g) L+2 orbital of **Pyrro-II**



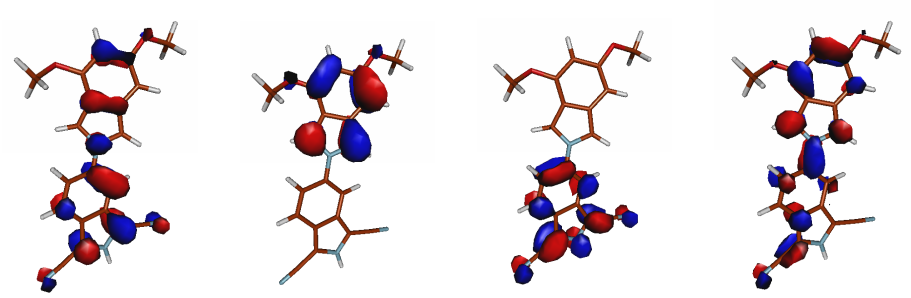
(h) L+3 orbital of **Pyrro-II**



(i) L+4 orbital of **Pyrro-II**

Figure S7: Relevant orbitals of **Pyrro-II**, computed at the ADC(2) level of theory.

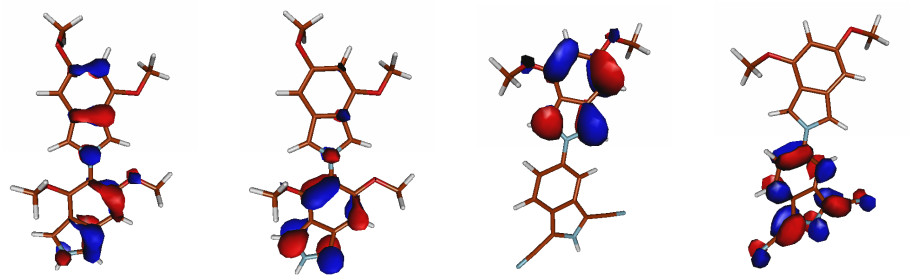
S2.3 Isoindole-I



(a) H-1 orbital of **Isoindole-I** (b) HOMO orbital of **Isoindole-I** (c) LUMO orbital of **Isoindole-I** (d) L+1 orbital of **Isoindole-I**

Figure S8: Relevant orbitals of **Isoindole-I**, computed at the ADC(2) level of theory.

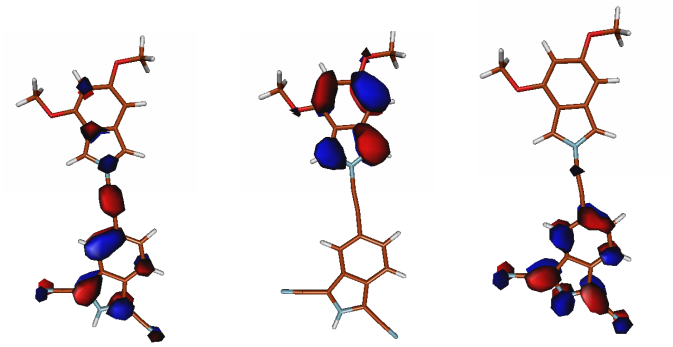
S2.4 Isoindole-II



(a) H-2 orbital of **Isoindole-II** (b) H-1 orbital of **Isoindole-II** (c) HOMO orbital of **Isoindole-II** (d) LUMO orbital of **Isoindole-II**

Figure S9: Relevant orbitals of **Isoindole-II**, computed at the ADC(2) level of theory.

S2.5 Isoindole-I-CC



(a) H-1 orbital of **Isoindole-I-CC** (b) HOMO orbital of **Isoindole-I-CC** (c) LUMO orbital of **Isoindole-I-CC**

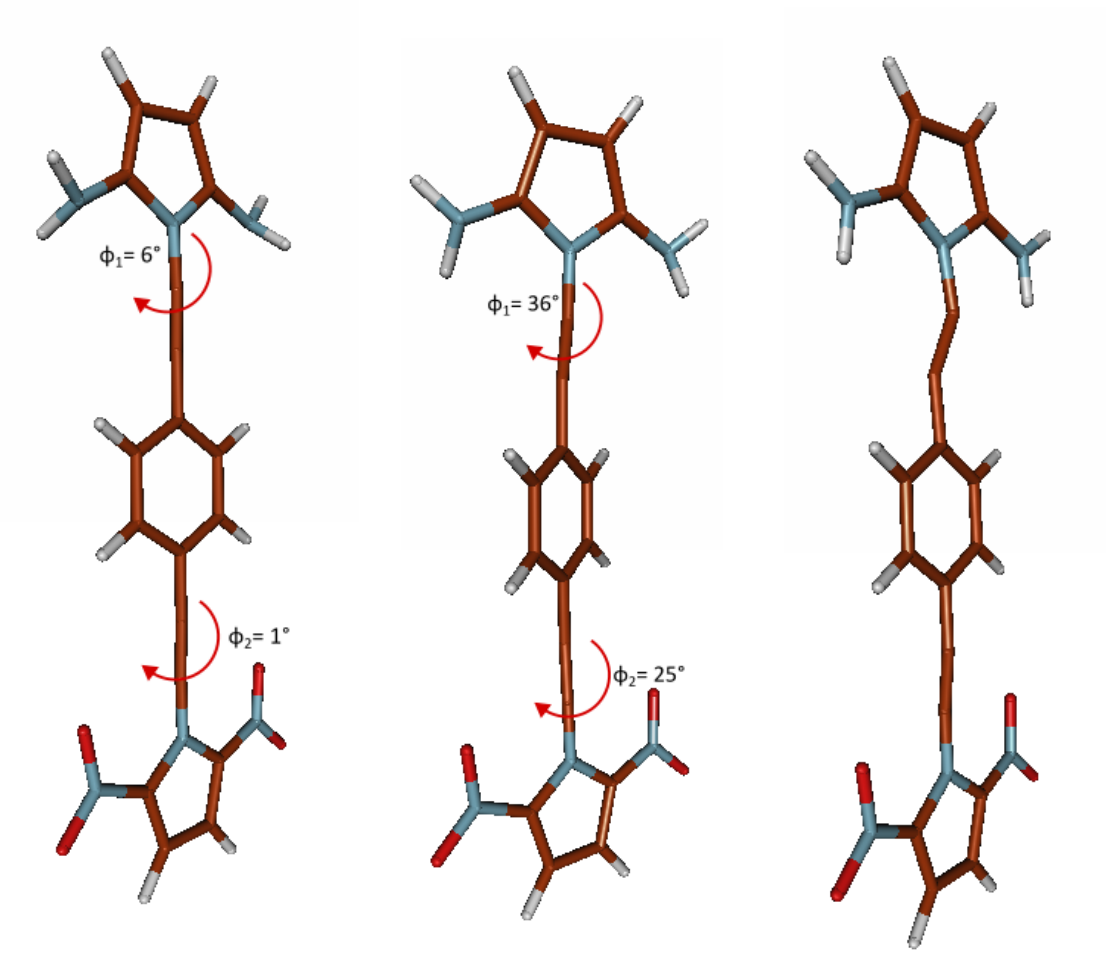
Figure S10: Relevant orbitals of **Isoindole-I-CC**, computed at the ADC(2) level of theory.

S3 HOMO and LUMO energies of the PMWs

Table S1: HOMO and LUMO energies (ϵ) of the studied **PMWs** determined at the ODM2/MRCI-SD level.

System	ϵ_{HOMO} (eV)	ϵ_{LUMO} (eV)
pyrro-I	-7.65	-1.54
pyrro-II	-6.86	-1.88
Isoindole-I	-7.30	-0.79
Isoindole-II	-6.53	0.73
Isoindole-I-CC	-7.21	-0.73

S4 Geometrical analysis of pyrro-I



(a) Optimized parallel ground-state minimum of **pyrro-I**.

(b) Optimized rotated ground-state minimum of **pyrro-I**.

(c) Optimized S_1 minimum of **pyrro-I**.

Figure S11: Optimized structure of ground and excited-state minima of **pyrro-I**.

Table S2: S_1 and S_2 energies and oscillator strengths at the three optimized minima of **pyrro-I**.

Conformation	**pyrro-I S0-min**	**pyrro-I S0-min-rot**	**pyrro-I S1-min**
E_{S1} (eV)	3.70	3.59	1.76
E_{S2} (eV)	4.01	3.85	2.81
f_{S1}	0.3857	0.0013	0.0009
f_{S2}	0.0043	0.3774	0.0133

S5 Benchmark ADC(2) calculations

Table S3: ADC(2) vertical excitation energies (E) and wavelengths (λ), oscillator strengths, excitation characters and state dipole moments of the relevant excited states of **pyrro-I** and **pyrro-II**, along with the leading orbital contributions, computed at the ground-state minima optimized with ODM2/MRCI-SD.

State	E/λ [eV/nm]	Exciation character	f	μ [D]
pyrro-I				
S1	3.20/387	Mixed CT/LE: H-1-L (86%)	0.6564	-21.0
S2	3.28/378	Mixed CT/LE: H-8-L (26%), H-14-L (23%)	0.0031	-3.9
S3	3.50/3.54	CT: H-L (86%)	0.0030	-48.2
pyrro-II				
S1	2.54/506	Mixed CT/LE: H-L+2 (52%), H-L (43%)	0.0077	-24.6
S2	3.05/407	Mixed CT/LE: H-L (53%), H-L+2 (39%)	0.0045	-32.0
S3	3.17	LE: H-1-L (23%), H-17-L (18%), H-2-L (14%)	0.0736	1.5
S4	3.39	Mixed CT/LE: H-L+4 (58%), H-L+5 (38%)	0.0001	-12.3
S5	3.48	LE: H-19-L (49%), H-17-L+1 (19%)	0.0003	5.7

Table S4: ADC(2) vertical excitation energies (E) and wavelengths (λ), oscillator strengths, excitation characters and state dipole moments of the relevant excited states of **isoindole-I**, **isoindole-II** and **isoindole-I-CC**, computed at the ground-state minima optimized with ODM2/MRCI.

State	E/λ [eV/nm]	Exciation character	f	μ [D]
Isoindole-I				
S1	3.18/390	CT: H-L (86%)	0.0501	-21.2
S2	3.80/326	Mixed CT/LE: H-1-L (79%)	0.2275	-9.8
S3	4.01/309	Mixed CT/LE: H-L+1 (73%)	0.0240	-10.2
Isoindole-II				
S1	3.66/338	CT: H-L (88%)	0.1089	-5.5
S2	4.09/303	LE: H-1-L (87%)	0.1625	9.7
S3	4.30/288	Mixed CT/LE: H-2-L (79%)	0.3279	6.4
Isoindole-I-CC				
S1	3.59/349	CT: H-L (62%), H-1-L (23%)	0.1760	-25.5
S2	3.93/315	Mixed CT/LE: H-1-L (79%)	0.3508	-14.1

Table S5: S_0-S_1 energy gap (ΔE), S_0-S_1 oscillator strengths (f) and the S_1 excitation character computed at the ODM2/MRCI-optimized S_1 geometries of all studied systems, at the ADC(2) level of theory.

PMW	Δ E S_0-S_1 [eV]	f	S_1 character
pyrro-I	1.15	0.0009	H-L (78 %)
pyrro-II	0.15	0.0000	H-L (88 %)
isoindole-I	2.52	0.0673	H-L (91%)
isoindole-II	2.77	0.0616	H-L (94 %)
isoindole-I-CC	1.26	0.0196	H-L (88 %)

S6 Nuclear ensemble absorption spectra

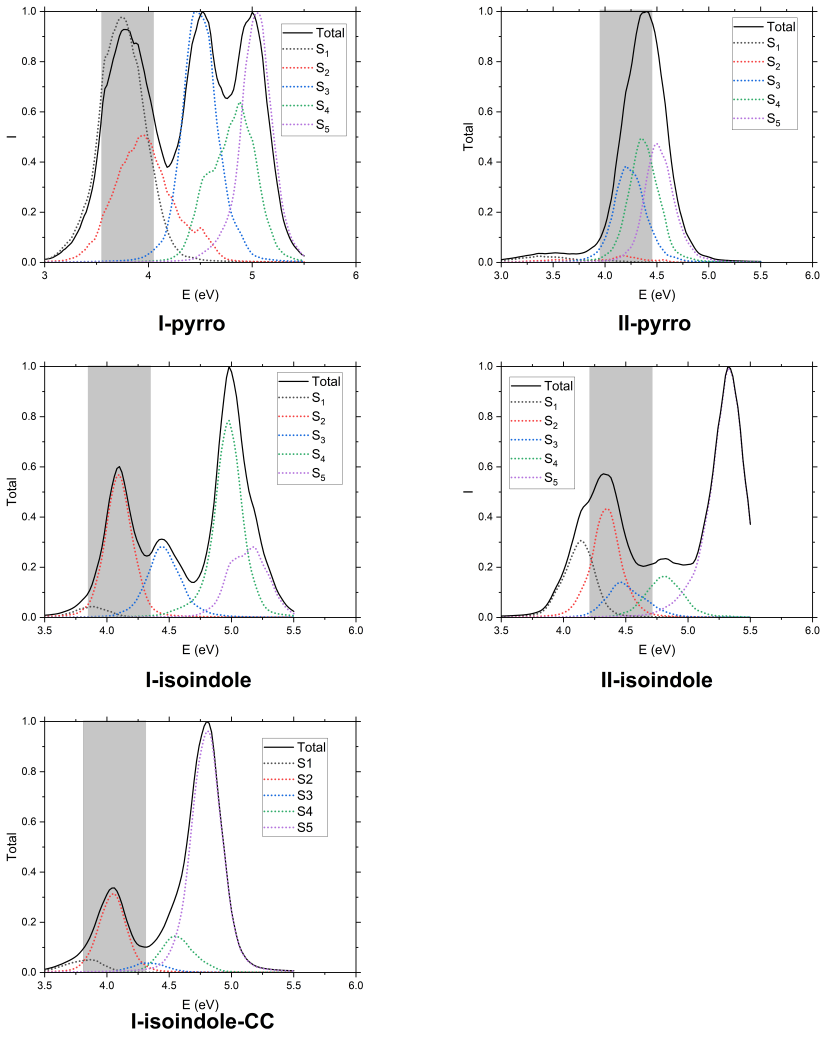


Figure S12: Nuclear ensemble absorption spectra of the studied systems. Full black line denote the total simulated absorption spectrum, while dotted lines represent contributions from transitions to given adiabatic states. The contributions from states S_1 to S_5 have been marked black, red, blue, green and violet lines, respectively.