A LINEAR MODELS APPROACH TO OPTIMIZE CARBAZOLE-BASED DYES FOR SOLAR CELL APPLICATIONS

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DFT approach to selected modified dyes

The molecular structures of all molecules were optimized using Density Functional Theory (DFT) with the B3LYP functional and the 6-311G(d, p) basis set. Based on these optimized structures, the first 15 excited states were calculated using the CAM-B3LYP functional and the same basis set employed for the optimization. The ground and excited states for all molecules were obtained considering the solvent effect (chloroform) using the Conductor-like Polarizable Continuum Model (CPCM).

To simulate the interaction between the dyes and the semiconductor, we used the $(TiO_2)_9$ cluster due to its proven utility in other computational studies [1–5]. We considered the same bidentate binding mode because of its frequently reported stability [2–4]. Subsequently, the Dyes@$(TiO_2)_9$ systems were optimized using the B3LYP functional with the 6-311G(d, p) and LANL2DZ basis sets, applying the latter exclusively to Ti atoms. The first 15 excited states were then calculated using the CAM-B3LYP functional and the two aforementioned basis sets. In addition, the solvent effect (chloroform) was considered in both calculations via the CPCM model.

Parameters related to photovoltaic properties

In DSSC research, it is notable that a significant amount of work has employed computational methods to evaluate potential new sensitizers, with Density Functional Theory (DFT) being the most frequent approach. This method is commonly used to explore parameters related to DSSC performance, such as J_{SC} and V_{OC} [6–8]. For instance, J_{SC} (Eq. S1) is related to the elementary charge, q, charge collection efficiency, η_{coll}, electron injection efficiency, η_{inj}, light-harvesting efficiency, LHE(λ), and the photon flux from incident radiation, $I_S(\lambda)$.

$$J_{SC} = q \int \mathrm{LHE}(\lambda) \times \eta_{inj} \times \eta_{coll} \times I_S(\lambda) d\lambda \qquad \text{Eq. S1}$$

In this equation, the LHE(λ) and η_{inj} can be evaluated by DFT methods. For example, a commonly employed approximation for LHE(λ) involves only the oscillator strength, f, associated with the maximum absorption of the dye (Eq. S2).

$$\mathrm{LHE} = 1 - 10^{-f} \qquad \text{Eq. S2}$$

On the other hand, because directly estimating η_{inj} requires obtaining kinetic parameters related to charge injection and intramolecular decay [9,10], this term is

commonly assessed indirectly via the injection free energy, ΔG_{inj}, given their well-established satisfactory relationship $(\eta_{inj} \propto \Delta G_{inj})$ [9,10]. In this regard, ΔG_{inj} is readily obtained since it depends exclusively on the conduction band energy of the semiconductor, E_{CB} (-4.0 eV for TiO_2), and the oxidation potential of the dye in the excited state, E^*_{Dye} (Eq. S3). Where E^*_{Dye} depends on the vertical excitation energy for the maximum absorption, $E_{\lambda_{max}}$, and the oxidation potential of the dye in the ground state, E_{Dye}, which is essentially the negative of the HOMO energy (Eq. S4).

$$\Delta G_{inj} = E^*_{Dye} - E_{CB} \quad \text{Eq. S3}$$

$$E^*_{dye} = E_{Dye} - E_{\lambda_{max}} \quad \text{Eq. S4}$$

A parameter related to the regeneration of the oxidized dye can also be estimated by obtaining the change in the regeneration free energy, ΔG_{reg}, a commonly used approach expressed by Equation S5. Here, $E_{I_3^-/I^-}$ corresponds to the redox potential of the I_3^-/I^- couple (-4.8 eV).

$$\Delta G_{reg} = E_{I_3^-/I^-} - E_{Dye} \quad \text{Eq. S5}$$

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Others result of free Dyes and Dye@(TiO2)$_9$ systems

Structurally, all optimized complexes exhibit Ti–O bond lengths consistent with those obtained in other reported studies [11,12], falling within the range of 2.0 to 2.2 Å (see Table S1). Furthermore, given the negative energy for the interaction between the sensitizer and the (TiO2)$_9$, E_{bind} (Eq. S6), it follows that the formation of the Dye@(TiO2)$_9$ complex is favorable.

$$E_{bind} = E_{Dye@(TiO2)9} - (E_{Dye} + E_{(TiO2)9}) \quad \text{Eq. S6}$$

Table S1 – Bond lengths and interaction energy for the formation of the Dye@(TiO_2)$_9$ clusters.

Molecule	Ti-O1	Ti-O2	Energy bind(eV)
LY-F	2.192	2.055	-1.384
LY-P	2.059	2.245	-1.268
LY-S	2.180	2.073	-1.351
A1A2	2.071	2.194	-1.261
A1A5	2.148	2.096	-1.386
A1A6	2.163	2.069	-1.457
A3A1	2.175	2.091	-1.365
A3A4	2.149	2.091	-1.387
A6A3	2.173	2.092	-1.420

Figure S1. Frontiers molecular orbitals of HOMO and LUMO of the complexes Dye@(TiO2)$_9$.

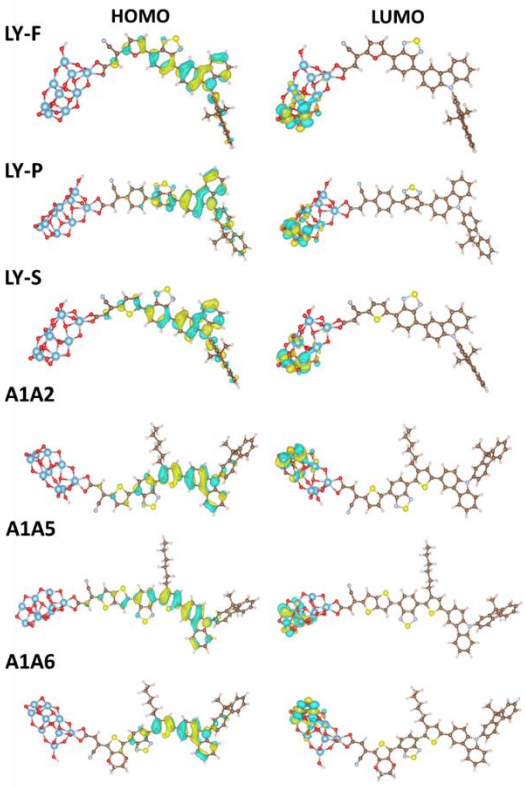


Table S2 – Energy (eV) of the HOMO. LUMO. and Gap for the Dye@$(TiO_2)_9$ clusters.

Molecule	HOMO	LUMO	*GAP*
LY-F	-5.612	-3.455	2.157
LY-P	-5.606	-3.515	2.091
LY-S	-5.632	-3.464	2.167
A1A2	-5.437	-3.514	1.923
A1A5	-5.403	-3.478	1.924
A1A6	-5.444	-3.445	1.999

Table S3 – Absorption λ_{max}, oscillator strength and main compositions to Dye@$(TiO_2)_9$.

Molecule	λ (nm)	f	Main Compositions*
LY-F	482.59	1.405	H-1 → L (15.52%) H → L (48.41%) H → L+1 (11.71%)
LY-P	411.67	1.235	H → L+2 (13.31%) H → L+3 (15.02%) H → L+8 (14.47%) H → L+9 (16.13%)
LY-S	464.02	1.530	H-1 → L (12.70%) H → L (38.90%) H → L+1 (13.83%)
A1A2	499.49	1.596	H-1 → L (18.97%) H → L (53.43%)
A1A5	502.62	2.033	H-1 → L (15.24%) H → L (42.14%)
A1A6	449.07	1.497	H-1 → L+1 (13.73%) H → L+1 (18.00%) H → L+2 (10.40%)

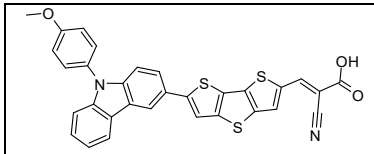
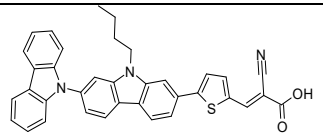
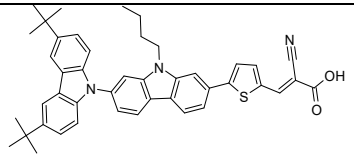
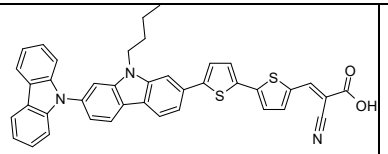
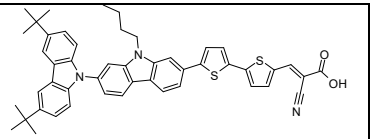
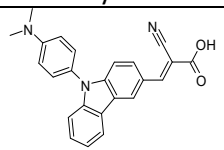
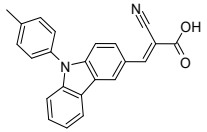
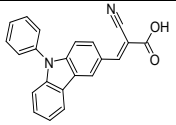
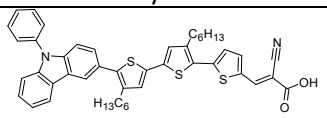
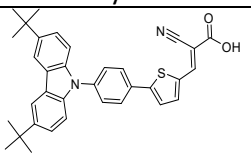
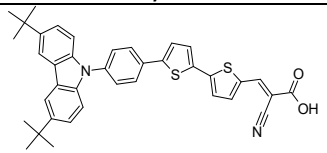
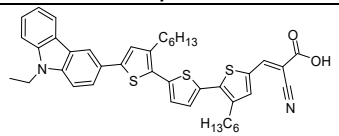
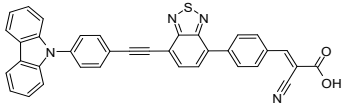
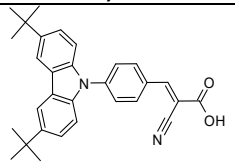
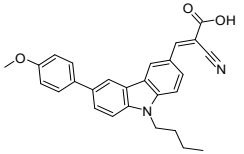
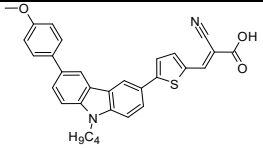
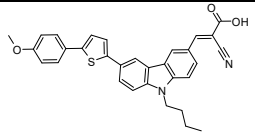
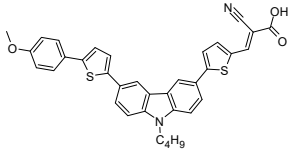
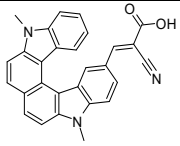
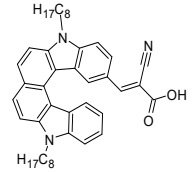
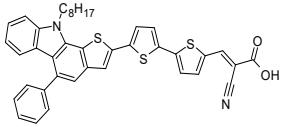
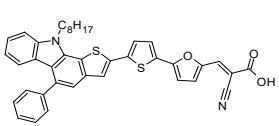
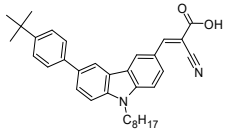
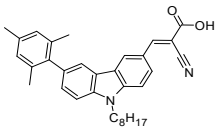
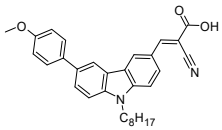
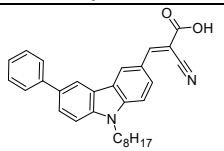
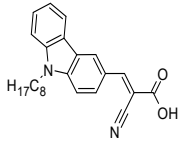
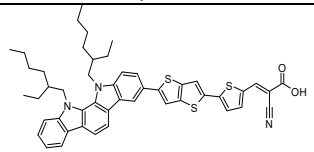
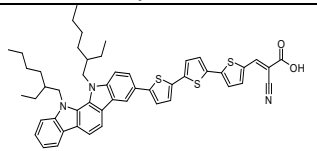
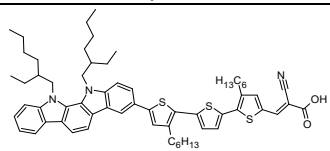
* H: HOMO, L: LUMO

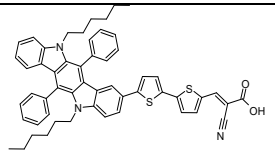
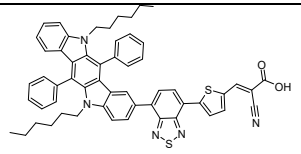
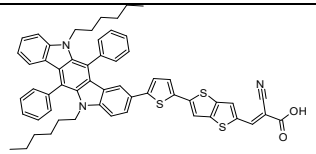
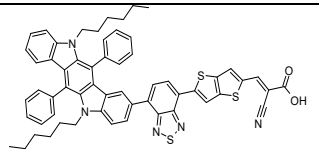
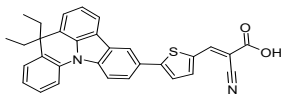
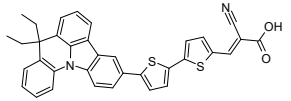
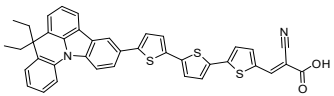
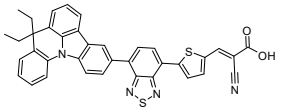
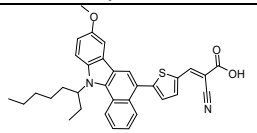
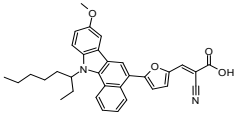
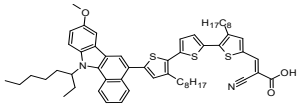
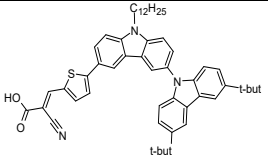
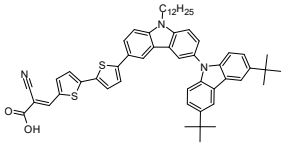
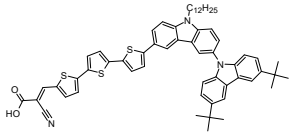
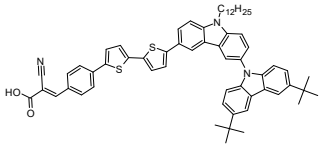
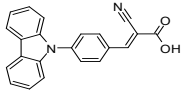
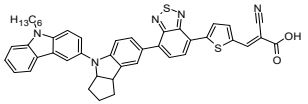
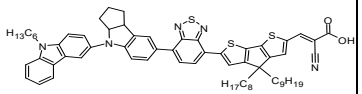
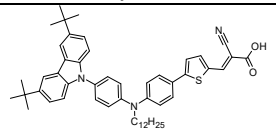
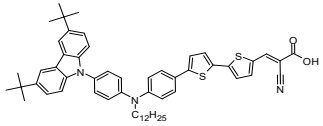
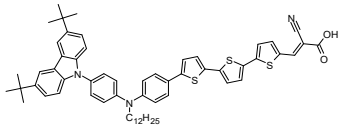
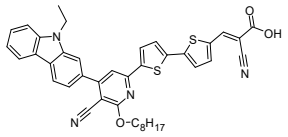
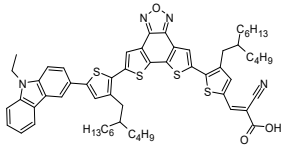
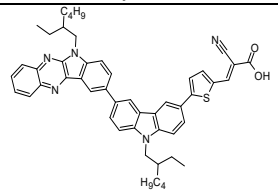
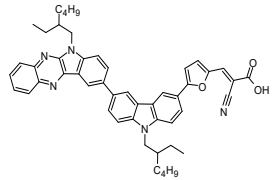
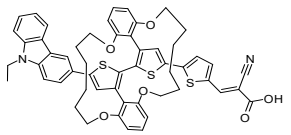
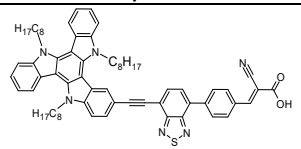
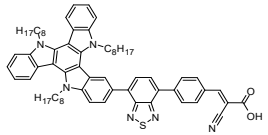
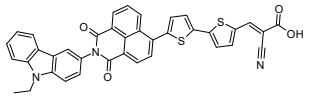
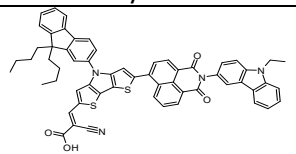
Table S5. Dye Structures and Photovoltaic Performances

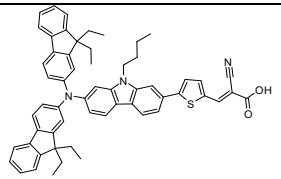
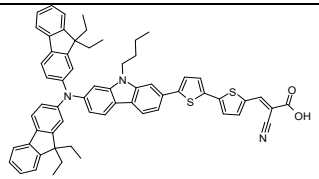
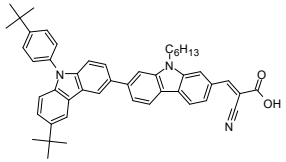
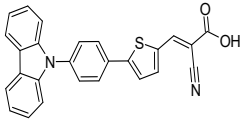
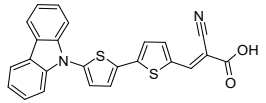
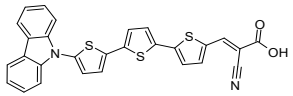
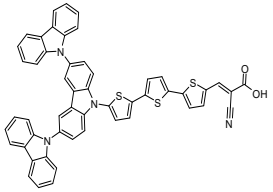
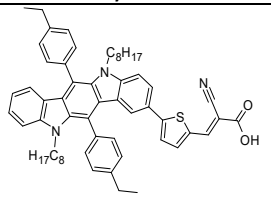
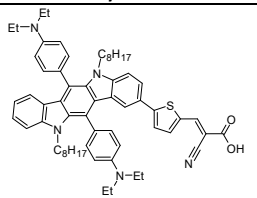
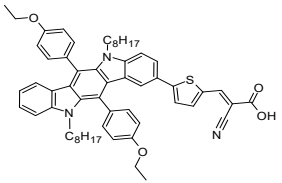
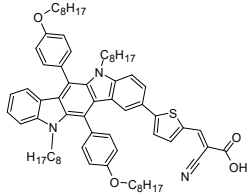
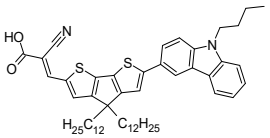
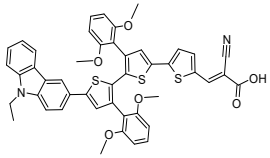
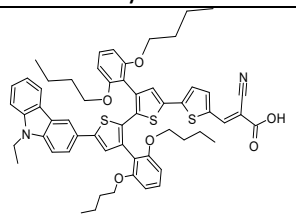
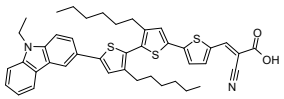
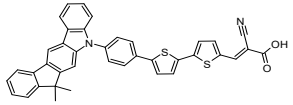
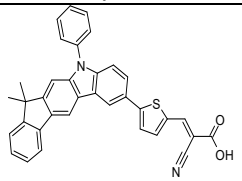
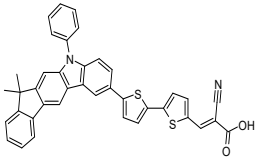
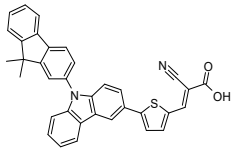
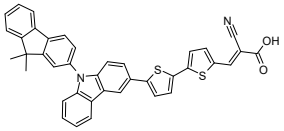
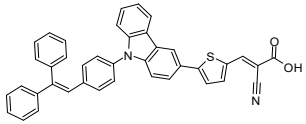
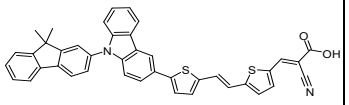
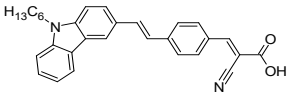
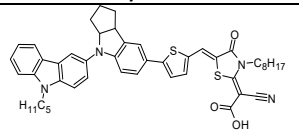
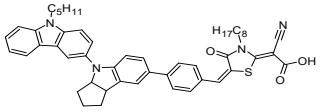
Dye	%PCE	Sol.	doi	Dye	%PCE	Sol.	doi
1.	5.64	Et	10.1016/j.tet.2013.02.058	**33.**	4.11	THF	10.1039/C3TA11748K
2.	4.22	Di	10.1021/am404948w	**34.**	6.40	THF	10.1039/C3TA11748K
3.	4.95	Di	10.1021/am404948w	**35.**	5.43	THF	10.1039/C3TA01657A
4.	6.04	Di	10.1021/am404948w	**36.**	6.50	THF	10.1039/C3TA01657A
5.	5.48	Di	10.1021/am404948w	**37.**	2.96	THF	10.1039/C3TA01657A
6.	1.21	Ac	10.1108/PRT-09-2014-0077	**38.**	4.61	THF	10.1039/C3TA01657A
7.	2.82	Ac	10.1108/PRT-09-2014-0077	**39.**	6.01	Di	10.1021/am508400a
8.	3.69	Ac	10.1108/PRT-09-2014-0077	**40.**	6.93	Di	10.1021/am508400a
9.	5.92	Ac	10.1016/j.jpowsour.2020.227776	**41.**	7.54	Di	10.1021/am508400a
10.	2.39	Tr	doi.org/10.1021/jp1055842	**42.**	3.64	Di	10.1002/ejoc.201300373
11.	2.48	Tr	doi.org/10.1021/jp1055842	**43.**	4.80	Di	10.1002/ejoc.201300373
12.	7.44	Tr	10.1016/j.electacta.2018.08.068	**44.**	5.69	Di	10.1002/ejoc.201300373
13.	3.50	Tr	10.1016/j.dyepig.2016.08.013	**45.**	4.62	Di	10.1002/ejoc.201300373
14.	2.68	Ac	10.1246/cl.2010.864	**46.**	1.77	Di	10.1016/j.dyepig.2012.03.028
15.	1.87	Di	10.1002/ejoc.201600353	**47.**	5.13	Di	10.1021/acsami.5b08888
16.	4.54	Di	10.1002/ejoc.201600353	**48.**	7.69	Di	10.1021/acsami.5b08888
17.	2.52	Di	10.1002/ejoc.201600353	**49.**	3.52	Di	10.1021/jp304489t
18.	4.57	Di	10.1002/ejoc.201600353	**50.**	4.10	Di	10.1021/jp304489t
19.	2.49	Tr	10.1016/j.solmat.2009.11.014	**51.**	5.12	Di	10.1021/jp304489t
20.	3.18	Tr	10.1016/j.solmat.2009.11.014	**52.**	3.34	Di	10.1016/j.solener.2018.09.073
21.	6.60	Tr	10.1016/j.tet.2014.01.001	**53.**	5.98	THF	10.1021/am5067145
22.	6.73	Tr	10.1016/j.tet.2014.01.001	**54.**	6.48	Di	10.1016/j.jpowsour.2015.01.148
23.	2.17	Tr	10.1039/C6RA01185C	**55.**	7.03	Di	10.1016/j.jpowsour.2015.01.148
24.	0.98	Tr	10.1039/C6RA01185C	**56.**	9.20	Di	10.1039/C3TA12368E
25.	2.69	Tr	10.1039/C6RA01185C	**57.**	7.15	Di	10.1039/C7NJ04629D
26.	0.98	Tr	10.1039/C6RA01185C	**58.**	7.26	Di	10.1039/C7NJ04629D
27.	1.11	Tr	10.1039/C6RA01185C	**59.**	0.57	Di	10.1007/s10854-018-9750-4
28.	5.78	Tr	10.1016/j.dyepig.2019.01.033	**60.**	0.92	Di	10.1007/s10854-018-9750-4
29.	5.23	Tr	10.1016/j.dyepig.2019.01.033	**61.**	6.44	Di	10.1016/j.dyepig.2015.07.034
30.	5.97	Tr	10.1016/j.dyepig.2019.01.033	**62.**	4.77	Di	10.1016/j.dyepig.2015.07.034
31.	6.09	THF	10.1039/C3TA11748K	**63.**	4.38	Di	10.1016/j.dyepig.2015.09.004
32.	5.55	THF	10.1039/C3TA11748K	**64.**	2.74	Di	10.1016/j.dyepig.2013.09.025

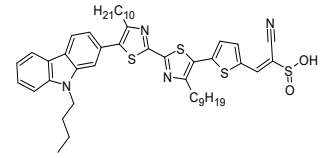
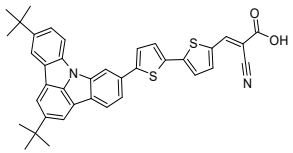
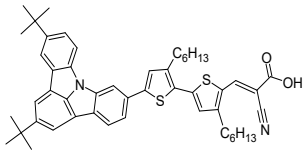
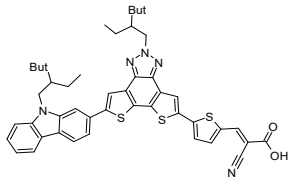
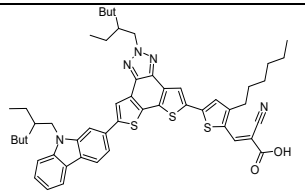
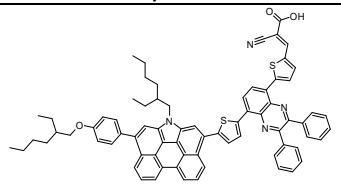
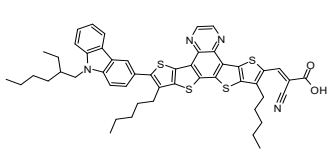
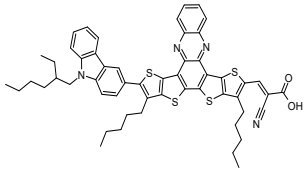
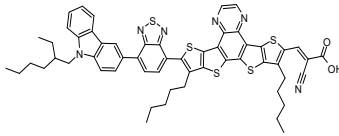
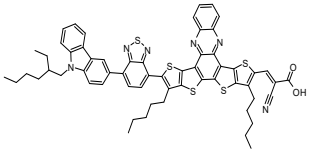
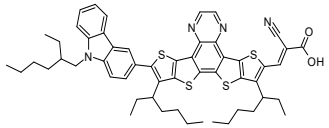
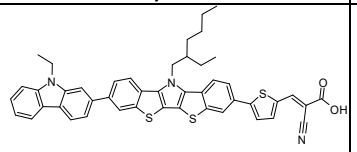
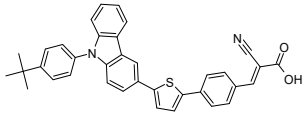
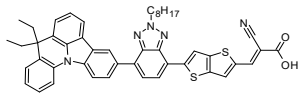
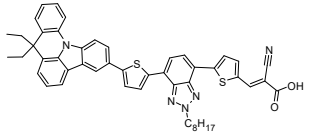
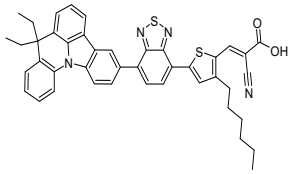
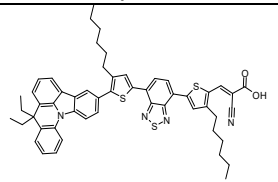
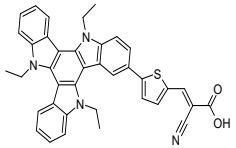
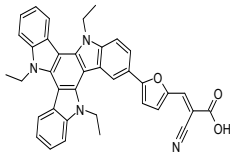
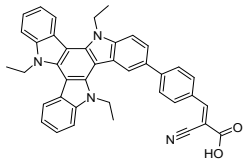
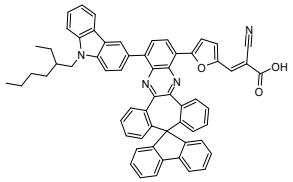
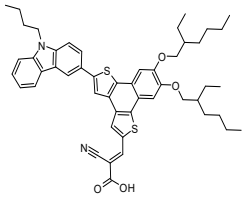
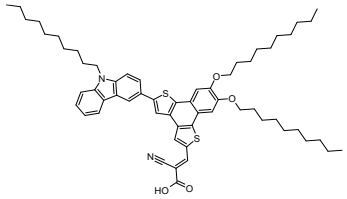
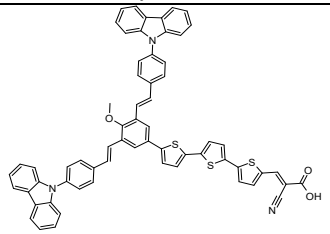
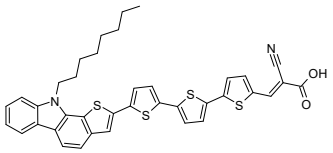
65.	2.94	Di	10.1016/j.dyepig.2013.09.025	**96.**	5.23	THF	10.1016/j.dyepig.2018.06.010
66.	4.30	Di	10.1016/j.dyepig.2013.09.025	**97.**	5.30	THF	10.1016/j.dyepig.2018.10.004
67.	4.86	Di	10.1016/j.dyepig.2013.09.025	**98.**	5.65	THF	10.1039/C3RA43057J
68.	6.25	Di	10.1016/j.jpowsour.2016.04.043	**99.**	6.23	THF	10.1039/C3RA43057J
69.	8.09	Di	10.1016/j.jpowsour.2016.04.043	**100.**	7.15	THF	10.1039/C3RA43057J
70.	6.98	Di	10.1016/j.jpowsour.2016.04.043	**101.**	5.20	THF	10.1039/C3RA43057J
71.	7.58	Di	10.1016/j.jpowsour.2016.04.043	**102.**	5.82	THF	10.1039/C3RA43057J
72.	7.50	Di	10.1039/C3RA22249G	**103.**	6.10	THF	10.1021/ol402931u
73.	7.01	Di	10.1039/C9TC01520E	**104.**	5.50	THF	10.1021/ol402931u
74.	8.01	Di	10.1039/C9TC01520E	**105.**	5.11	THF	10.1021/ol402931u
75.	5.06	Di	10.1039/C9TC01520E	**106.**	4.87	Di	10.1002/gch2.201900034
76.	4.23	DMF	10.1039/C7PP00350A	**107.**	4.49	THF	10.1039/C3TA12901B
77.	5.97	DMF	10.1039/C7PP00350A	**108.**	4.60	THF	10.1039/C3TA12901B
78.	5.34	DMF	10.1039/C7PP00350A	**109.**	3.03	THF	10.1002/asia.201402654
79.	5.02	Et	10.1016/j.tet.2006.12.082	**110.**	5.9	Tr	10.1039/C4QO00285G
80.	5.15	Et	10.1016/j.tet.2006.12.082	**111.**	6.5	Tr	10.1039/C4QO00285G
81.	3.87	Et	10.1016/j.tet.2006.12.082	**112.**	7.0	Tr	10.1039/C4QO00285G
82.	3.76	Et	10.1016/j.tet.2006.12.082	**113.**	4.31	Et	10.1021/jp906334w
83.	7.1	Et	10.1039/C5TA06548H	**114.**	5.96	Tr	10.1016/j.tet.2015.04.018
84.	8.48	Met	10.1016/j.dyepig.2018.03.072	**115.**	5.2	Di	10.1016/j.dyepig.2015.02.020
85.	4.69	Met	10.1016/j.dyepig.2018.03.072	**116.**	6.5	Di	10.1016/j.dyepig.2015.02.020
86.	4.65	THF	10.1016/j.dyepig.2012.10.002	**117.**	6.5	Di	10.1016/j.dyepig.2015.02.020
87.	3.96	THF	10.1039/C5RA02720A	**118.**	6.95	Di	10.1039/C4TA05162A
88.	2.85	THF	10.1039/C5RA02720A	**119.**	6.67	Di	10.1039/C4TA05162A
89.	7.52	THF	10.1039/C6TA02275H	**120.**	2.30	Di	10.1021/jo200501b
90.	8.51	THF	10.1039/C6TA02275H	**121.**	3.19	Di	10.1016/j.tetlet.2014.04.037
91.	7.58	THF	10.1016/j.dyepig.2016.12.013	**122.**	5.10	Di	10.1021/am500947k
92.	6.48	THF	10.1016/j.dyepig.2018.06.010	**123.**	4.90	Di	10.1002/cssc.201200975
93.	6.33	THF	10.1016/j.dyepig.2018.06.010	**124.**	5.80	Di	10.1002/cssc.201200975
94.	7.77	THF	10.1016/j.dyepig.2018.06.010	**125.**	5.80	Di	10.1002/cssc.201200975
95.	5.23	THF	10.1016/j.dyepig.2018.06.010	**126.**	5.60	Di	10.1002/cssc.201200975

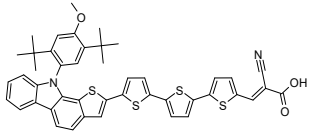
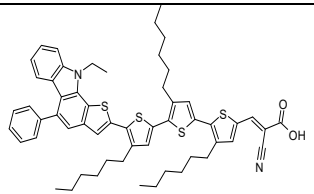
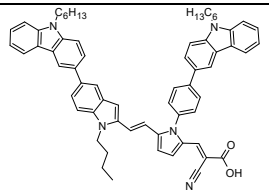
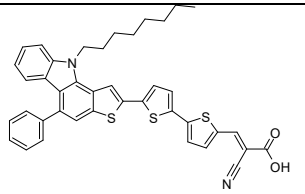
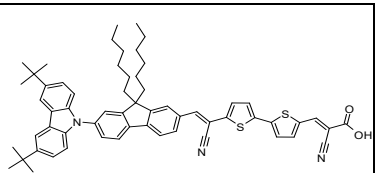
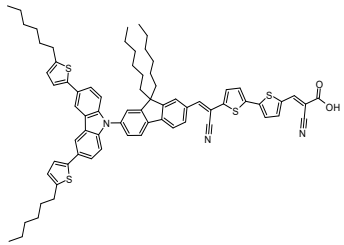
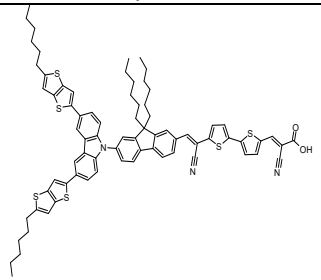
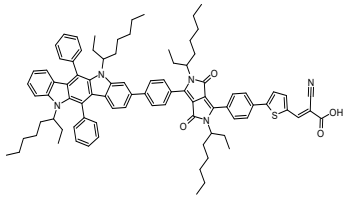
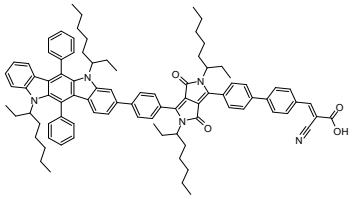
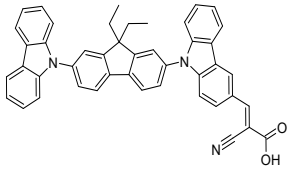
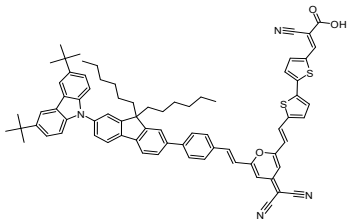
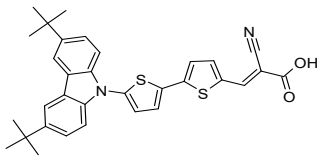
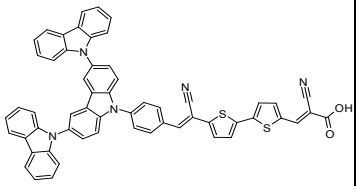
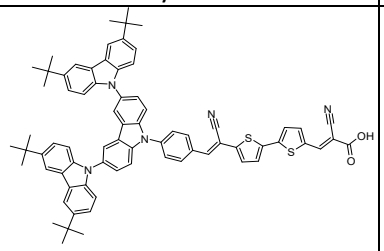
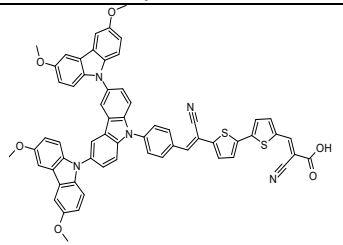
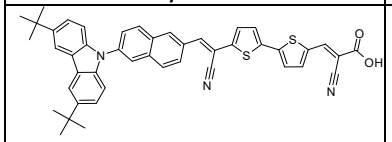
Ac – Acetonitrile; **Et –** Ethanol; **Di –** Dichloromethane; **DMF -** Dimethylformamide**; Met** – Methanol**; Tr –** Trichloromethane; **THF** – Tetrahydrofuran;

 dye1	 dye2	 dye3	 dye4	 dye5
 dye6	 dye7	 dye8	 dye9	 dye10
 dye11	 dye12	 dye13	 dye14	 dye15
 dye16	 dye17	 dye18	 dye19	 dye20
 dye21	 dye22	 dye23	 dye24	 dye25
 dye26	 dye27	 dye28	 dye29	 dye30

 dye31	 dye32	 dye33	 dye34	 dye35
 dye36	 dye37	 dye38	 dye39	 dye40
 dye41	 dye42	 dye43	 dye44	 dye45
 dye46	 dye47	 dye48	 dye49	 dye50
 dye51	 dye52	 dye53	 dye54	 dye55
 dye56	 dye57	 dye58	 dye59	 dye60

 dye61	 dye62	 dye63	 dye64	 dye65
 dye66	 dye67	 dye68	 dye69	 dye70
 dye71	 dye72	 dye73	 dye74	 dye75
 dye76	 dye77	 dye78	 dye79	 dye80
 dye81	 dye82	 dye83	 dye84	 dye85

 dye86	 dye87	 dye88	 dye89	 dye90
 dye91	 dye92	 dye93	 dye94	 dye95
 dye96	 dye97	 dye98	 dye99	 dye100
 dye101	 dye102	 dye103	 dye104	 dye105
 dye106	 dye107	 dye108	 dye109	 dye110

 dye111	 dye112	 dye113	 dye114	 dye115
 dye116	 dye117	 dye118	 dye119	 dye120
 dye121	 dye122	 dye123	 dye124	 dye125
 dye126				