

Supporting Information

Impact of Spin Exchange Interaction on Charge Transfer in Dual-Polymer Photovoltaic Composites

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SI-I. NIR-Vis-UV Spectra of Polymer Composites.

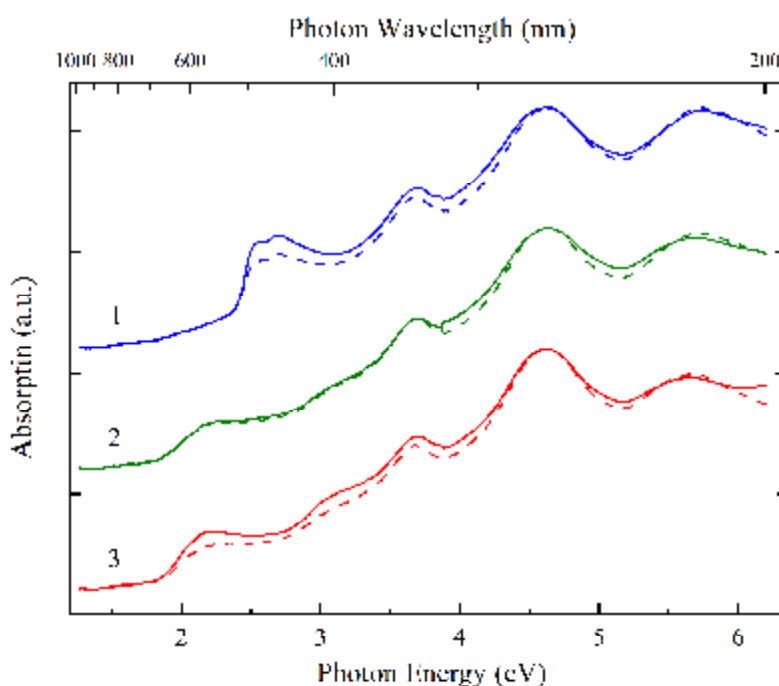


Figure S1. NIR-Vis-UV spectra of the F8T2:PC₆₁BM (1), PFO-DBT:PC₆₁BM (2), PCDTBT:PC₆₁BM (3) subsystems (dashed lines) as well as the PANI:TSA/F8T2:PC₆₁BM (1), PANI:TSA/PFO-DBT:PC₆₁BM (2), PANI:TSA/PCDTBT:PC₆₁BM (3) dual-polymer composites (solid lines), registered at $T = 298$ K.

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SI-II. DFT Evaluation of Morphology and Radical Spin Density Overdistribution in PCDTBT/PANI π - π Stacking Model Complex.

SI-IIa. Structures. FF and DFT setting.

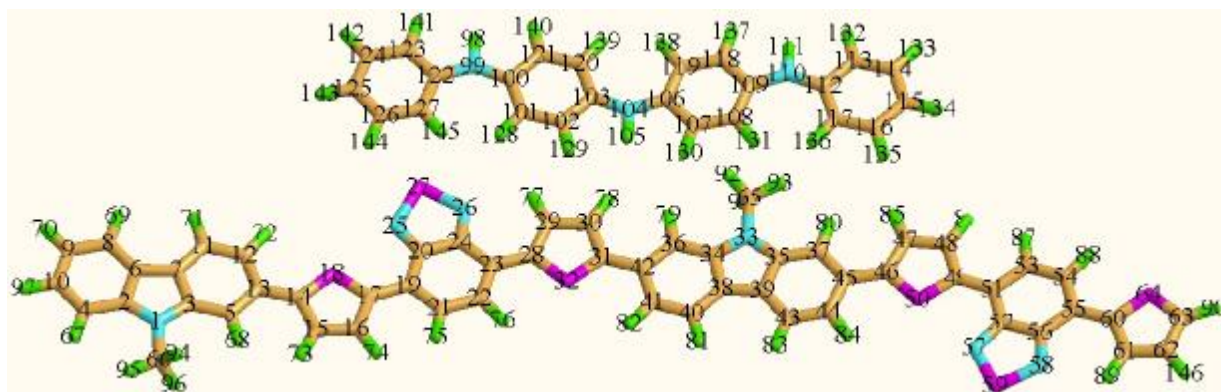


Figure S2. The denomination of the atom number of the π - π stacking 4ANI/2CDTBT complex after MM2 steric energy optimization. The atoms C- dark yellow, H- green, N- blue, O- red, S- violet in the structures are denominated in DFT hfc calculation after B3LYP/6-311G energy/structure optimization.

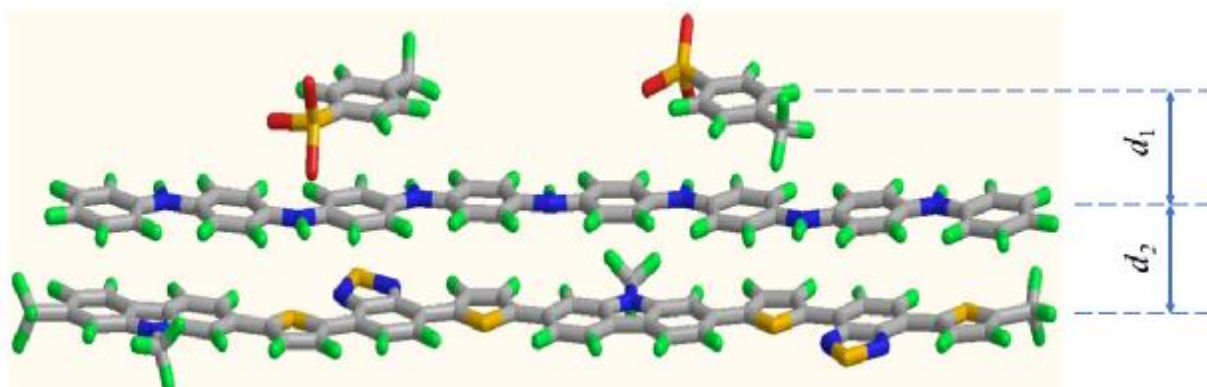
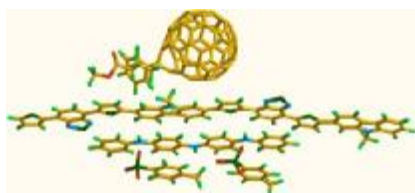


Figure S3. Model of the π - π stacking complex 8ANI:2TSA/2CDTBT after MM2 optimization, $d_1 \approx d_2 \approx 3.4 \pm 0.1$ Å.

SI-IIb. Cartesian coordinates data



**Table S1. The Complex Model
of 4ANI:2TSA / 2CDTBT:
PC₆₁BM (Only FF Energy /
Structure Optimistion)**

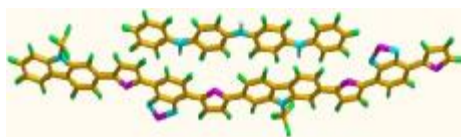
Atoms	X	Y	Z								
N(1)	6.348	5.471	3.238	H(74)	8.816	1.510	1.486	C(172)	27.084	-2.727	-3.499
C(2)	5.132	5.123	3.115	H(75)	11.137	5.356	3.086	C(173)	27.249	-4.147	-2.933
C(3)	7.179	4.594	2.844	H(76)	13.469	4.642	2.736	C(174)	28.578	-4.757	-3.352
C(4)	3.961	5.713	3.394	H(77)	15.148	3.606	2.264	O(175)	29.348	-5.025	-2.260
C(5)	8.518	4.554	2.798	H(78)	17.087	2.551	1.849	C(176)	30.625	-5.568	-2.497
C(6)	5.156	3.887	2.585	H(79)	17.047	-1.935	0.184	O(177)	28.899	-4.956	-4.502
C(7)	6.445	3.559	2.416	H(80)	19.457	-2.351	0.153	C(178)	19.654	-1.780	-5.034
C(8)	4.031	3.212	2.320	H(81)	21.515	-2.193	0.367	H(179)	27.587	-0.150	-5.268
C(9)	2.859	3.807	2.600	H(82)	26.726	-2.862	0.346	H(180)	29.595	1.143	-4.915
C(10)	2.826	5.042	3.131	H(83)	23.452	2.058	1.846	H(181)	30.010	2.221	-2.758
C(11)	7.040	2.465	1.934	H(84)	21.091	1.864	1.671	H(182)	28.378	1.977	-0.951
C(12)	8.384	2.439	1.894	H(85)	25.927	1.728	1.848	H(183)	26.360	0.690	-1.302
C(13)	9.161	3.466	2.316	H(86)	28.161	0.946	1.642	H(184)	25.976	-1.928	-1.833
C(14)	10.514	3.421	2.266	H(87)	28.663	-3.537	0.088	H(185)	24.971	-2.718	-3.060
C(15)	11.374	4.373	2.657	H(88)	31.117	-3.731	0.086	H(186)	27.997	-2.144	-3.230
C(16)	12.636	3.980	2.464	H(89)	33.108	-3.385	0.283	H(187)	27.018	-2.769	-4.611
C(17)	12.699	2.747	1.934	H(90)	35.329	-3.162	0.514	H(188)	27.163	-4.123	-1.822
S(18)	11.310	2.293	1.763	H(91)	37.152	0.953	2.158	H(189)	26.431	-4.805	-3.308
C(19)	13.821	2.047	1.627	H(92)	39.587	0.346	2.087	H(190)	31.109	-5.751	-1.511
C(20)	13.881	0.798	1.108	H(95)	39.870	-2.089	1.204	H(191)	30.537	-6.538	-3.036
C(21)	15.032	2.594	1.846	H(96)	23.405	-3.254	-0.860	H(192)	31.246	-4.845	-3.072
C(22)	16.189	1.963	1.595	H(97)	24.892	-3.837	-0.070	H(193)	16.742	-2.284	3.596
C(23)	16.265	0.710	1.099	H(98)	23.368	-3.831	0.859	N(194)	16.863	-1.307	3.971
C(24)	15.054	0.160	0.858	H(99)	7.418	6.611	4.691	C(195)	18.104	-1.048	4.110
N(25)	12.867	0.093	0.815	H(100)	7.382	7.326	3.024	C(196)	18.685	0.072	4.571
N(26)	14.893	-1.003	0.381	H(101)	5.950	7.429	4.086	C(197)	20.019	0.188	4.661
S(27)	13.262	-1.436	0.190	H(102)	1.853	5.511	3.353	C(198)	20.857	-0.804	4.303
C(28)	17.465	0.106	0.899	C(105)	22.155	2.586	-2.431	N(199)	22.097	-0.550	4.451
C(29)	17.740	-1.138	0.474	C(106)	22.940	1.515	-2.268	H(200)	22.216	0.425	4.831
C(30)	19.054	-1.376	0.458	C(107)	22.387	0.310	-2.078	C(201)	23.240	-1.091	4.291
C(31)	19.738	-0.300	0.871	C(108)	21.056	0.190	-2.050	C(202)	24.293	-0.324	4.633
S(32)	18.762	0.758	1.159	C(109)	20.261	1.266	-2.173	C(203)	25.561	-0.752	4.529
N(33)	24.191	-1.884	0.574	C(110)	20.816	2.476	-2.368	C(204)	25.856	-1.980	4.071
C(34)	23.225	-1.090	0.798	C(111)	20.298	3.311	-3.286	N(205)	26.999	-2.523	3.919
C(35)	25.335	-1.372	0.784	C(112)	19.209	2.941	-3.986	H(206)	26.875	-3.497	3.538
C(36)	21.895	-1.219	0.704	C(113)	18.651	1.731	-3.783	C(207)	28.240	-2.271	4.072
C(37)	26.591	-1.826	0.678	C(114)	19.182	0.885	-2.880	C(208)	29.067	-3.281	3.728
C(38)	23.776	0.063	1.199	C(115)	19.320	-0.424	-3.176	C(209)	30.401	-3.176	3.831
C(39)	25.103	-0.116	1.192	C(116)	18.900	-0.888	-4.365	C(210)	30.951	-2.042	4.285
C(40)	23.007	1.107	1.514	C(117)	18.346	-0.049	-5.261	C(212)	30.150	-1.025	4.631
C(41)	21.675	0.966	1.406	C(118)	18.230	1.262	-4.973	C(213)	28.816	-1.143	4.526
C(42)	21.080	-0.181	0.997	C(119)	18.520	2.185	-5.909	C(214)	24.802	-2.744	3.722
C(43)	26.114	0.698	1.505	C(120)	18.915	1.798	-7.136	C(215)	23.533	-2.318	3.831
C(44)	27.367	0.227	1.380	C(121)	19.019	0.488	-7.428	C(216)	20.278	-1.925	3.843
C(45)	27.646	-1.027	0.952	C(122)	18.741	-0.435	-6.489	C(217)	18.943	-2.039	3.749
C(46)	28.913	-1.479	0.799	C(123)	19.539	-1.511	-6.347	C(218)	15.719	-0.771	4.145
C(47)	29.300	-2.693	0.380	C(124)	20.600	-1.676	-7.155	C(219)	14.670	-1.557	3.825
C(48)	30.632	-2.791	0.379	C(125)	21.771	-2.105	-6.642	C(220)	13.401	-1.143	3.963
C(49)	31.214	-1.656	0.803	C(126)	21.915	-2.326	-5.320	C(221)	13.144	0.088	4.425
S(50)	30.128	-0.700	1.066	C(127)	20.840	-2.174	-4.531	C(223)	14.169	0.890	4.741
C(51)	32.542	-1.435	0.971	C(128)	21.283	-1.708	-3.354	C(224)	15.435	0.462	4.601
C(52)	33.123	-0.304	1.437	C(129)	20.494	-0.853	-2.674	H(225)	18.108	0.944	4.897
C(53)	33.427	-2.405	0.671	C(130)	22.633	-1.584	-3.394	H(226)	20.415	1.143	5.051
C(54)	34.754	-2.268	0.810	C(131)	23.035	-1.976	-4.640	H(227)	24.140	0.700	5.019
C(55)	35.352	-1.146	1.268	C(132)	24.066	-1.453	-5.351	H(228)	26.332	-0.039	4.841
C(56)	34.468	-0.170	1.578	C(133)	25.050	-0.647	-4.906	H(229)	28.672	-4.237	3.342
N(57)	32.484	0.733	1.791	C(134)	25.549	-0.626	-3.508	H(230)	31.049	-4.019	3.535
N(58)	34.803	0.965	2.032	C(135)	24.380	0.009	-2.845	H(233)	32.047	-1.944	4.364
S(59)	33.485	1.990	2.338	C(136)	24.069	1.314	-2.967	H(234)	30.595	-0.085	4.999
C(60)	36.705	-1.066	1.385	C(137)	24.345	2.134	-4.012	H(235)	28.239	-0.261	4.826
C(61)	37.465	-0.038	1.813	C(138)	24.741	1.738	-5.257	H(236)	24.953	-3.765	3.328
C(62)	38.770	-0.325	1.788	C(139)	24.932	0.458	-5.667	H(237)	22.762	-3.032	3.519
C(63)	38.911	-1.572	1.336	C(140)	24.407	0.068	-6.840	H(238)	20.855	-2.798	3.519
S(64)	37.618	-2.177	1.031	C(141)	23.848	0.919	-7.709	H(239)	18.550	-2.993	3.354
C(66)	23.959	-3.262	0.106	C(142)	22.756	0.569	-8.410	H(240)	14.819	-2.581	3.438
C(67)	6.790	6.767	3.785	C(143)	22.200	-0.640	-8.207	H(241)	12.566	-1.812	3.694
H(69)	3.904	6.723	3.828	C(144)	22.749	-1.478	-7.309	H(242)	12.104	0.438	4.538
H(70)	9.053	5.440	3.166	C(145)	23.858	-1.138	-6.640	H(245)	13.967	1.908	5.116
H(71)	4.058	2.201	1.885	C(146)	20.864	-0.763	-8.110	H(246)	16.208	1.185	4.883
H(72)	1.915	3.275	2.393	C(147)	20.083	0.327	-8.237	O(247)	18.970	-4.405	6.189
H(73)	6.447	1.607	1.580	C(148)	20.640	1.538	-8.440	S(248)	17.310	-4.439	6.230
				C(149)	21.978	1.661	-8.516	O(249)	16.709	-5.212	7.325
				C(150)	22.601	2.676	-7.883	O(250)	16.622	-4.314	4.939
				C(151)	23.753	2.210	-7.362	C(251)	16.600	-2.899	6.847
				C(152)	24.177	2.596	-6.142	C(252)	15.270	-2.727	6.936
				C(153)	23.454	3.513	-5.481	C(253)	14.756	-1.567	7.377
				C(154)	22.318	4.014	-6.004	C(254)	15.557	-0.550	7.737
				C(155)	21.243	4.205	-5.218	C(255)	16.886	-0.725	7.647
				C(156)	20.144	3.860	-5.915	C(256)	17.403	-1.885	7.214
				C(157)	19.131	3.219	-5.301	C(257)	14.989	0.767	8.209
				C(158)	20.538	3.473	-7.143	H(258)	14.577	-3.532	6.639
				C(159)	21.879	3.580	-7.199	H(259)	13.661	-1.451	7.430
				C(160)	19.919	2.446	-7.756	H(260)	17.566	0.097	7.929
				C(161)	21.324	3.931	-3.905	H(261)	18.498	-1.982	7.154
				C(162)	22.479	3.464	-3.390	H(262)	15.088	0.850	9.315
				C(163)	23.547	3.218	-4.175	H(263)	15.526	1.623	7.741
				C(164)	23.193	-0.596	-2.653	H(264)	13.912	0.880	7.950
				C(165)	26.806	0.220	-3.322	O(265)	28.064	-4.035	6.669
				C(166)	27.730	0.344	-4.293	S(266)	26.765	-5.045	6.442
				C(167)	28.853	1.055	-4.103	O(267)	26.463	-6.012	7.506
				C(168)	29.085	1.644	-2.921	O(268)	26.439	-5.350	5.045
				C(169)	28.189	1.511	-1.933	C(269)	25.207	-4.178	6.727
				C(170)	27.070	0.799	-2.136	C(270)	24.022	-4.760	6.471
				C(171)	25.836	-2.031	-2.932	C(271)	22.873	-4.106	6.703

C(272)	22.874	-2.860	7.205
C(273)	24.060	-2.279	7.457
C(274)	25.211	-2.928	7.223
C(275)	21.578	-2.128	7.457
H(276)	23.974	-5.785	6.066
H(277)	21.914	-4.604	6.480
H(278)	24.093	-1.253	7.859
H(279)	26.159	-2.409	7.439
H(280)	21.172	-2.404	8.456
H(281)	21.706	-1.023	7.424
H(282)	20.816	-2.388	6.689

C(29)	-3.655	-1.373	-2.662
C(30)	-2.324	-1.486	-2.644
C(31)	-1.862	-1.497	-1.385
S(32)	-3.022	-1.410	-0.486
N(33)	2.809	-1.782	-2.140
C(34)	1.709	-1.709	-1.507
C(35)	3.834	-1.832	-1.389
C(36)	0.430	-1.640	-1.899
C(37)	5.152	-1.914	-1.615
C(38)	2.029	-1.705	-0.207
C(39)	3.364	-1.781	-0.134
C(40)	1.076	-1.625	0.724
C(41)	-0.204	-1.558	0.315
C(42)	-0.569	-1.567	-0.990
C(43)	4.200	-1.803	0.908
C(44)	5.518	-1.879	0.660
C(45)	6.035	-1.940	-0.590
C(46)	7.367	-2.011	-0.822
C(47)	7.985	-2.073	-2.012
C(48)	9.313	-2.072	-1.860
C(49)	9.655	-2.003	-0.563
S(50)	8.408	-2.026	0.217
C(51)	10.907	-1.910	-0.052
C(52)	11.214	-1.799	1.259
C(53)	11.984	-1.903	-0.862
C(54)	13.244	-1.799	-0.411
C(55)	13.564	-1.686	0.896
C(56)	12.487	-1.690	1.711
N(57)	10.338	-1.774	2.183
N(58)	12.575	-1.587	2.975
S(59)	11.046	-1.589	3.716
C(60)	14.851	-1.580	1.317
C(61)	15.306	-1.462	2.580
C(62)	16.640	-1.381	2.624
C(63)	17.101	-1.444	1.374
S(64)	16.016	-1.577	0.405
C(65)	2.850	-1.792	-3.613
C(66)	-16.073	0.698	3.102
H(67)	-18.836	1.091	2.362
H(68)	-13.557	0.238	2.250
H(69)	-17.526	0.568	-2.356
H(70)	-19.862	0.983	-1.742
H(71)	-15.079	0.173	-2.406
H(72)	-12.777	-0.165	-1.940
H(73)	-11.533	-0.058	2.662
H(74)	-9.098	-0.447	2.471
H(75)	-7.195	-0.779	1.762
H(76)	-5.056	-1.087	1.075
H(77)	-4.192	-1.326	-3.617
H(78)	-1.742	-1.536	-3.574
H(79)	0.243	-1.647	-2.981
H(80)	5.483	-1.950	-2.660
H(81)	1.331	-1.611	1.795
H(82)	-0.946	-1.490	1.128
H(83)	3.818	-1.752	1.940
H(84)	6.158	-1.884	1.559
H(85)	7.524	-2.086	-3.008
H(86)	9.980	-2.081	-2.731
H(87)	11.885	-1.984	-1.956
H(88)	14.014	-1.810	-1.202
H(89)	14.730	-1.429	3.511
H(90)	18.162	-1.402	1.093
H(91)	2.392	-2.729	-4.005
H(92)	2.297	-0.917	-4.025

H(93)	3.877	-1.725	-4.030
H(94)	-15.395	1.530	3.401
H(95)	-17.050	0.887	3.596
H(96)	-15.681	-0.257	3.520
H(97)	-20.495	1.240	0.595
H(98)	-6.066	2.214	-3.024
N(99)	-6.123	2.262	-1.973
C(100)	-4.952	2.170	-1.476
C(101)	-4.581	2.182	-0.185
C(102)	-3.293	2.079	0.180
C(103)	-2.293	1.964	-0.716
N(104)	-1.122	1.894	-0.217
H(105)	-1.182	1.933	0.833
C(106)	0.099	1.799	-0.573
C(107)	0.990	1.779	0.436
C(108)	2.315	1.704	0.228
C(109)	2.832	1.637	-1.1010
N(110)	4.056	1.573	-1.362
H(111)	4.120	1.524	-2.412
C(112)	5.227	1.557	-0.856
C(113)	6.231	1.481	-1.755
C(114)	7.521	1.459	-1.385
C(115)	7.847	1.512	-0.087
C(116)	6.868	1.584	0.825
C(117)	5.581	1.607	0.442
C(118)	1.939	1.638	-2.019
C(119)	0.614	1.720	-1.811
C(120)	-2.663	1.944	-2.007
C(121)	-3.952	2.042	-2.372
C(122)	-7.338	2.399	-1.612
C(123)	-8.228	2.449	-2.626
C(124)	-9.546	2.594	-2.412
C(125)	-10.015	2.692	-1.161
C(126)	-9.152	2.642	-0.138
C(127)	-7.836	2.498	-0.365
H(128)	-5.302	2.274	0.635
H(129)	-3.076	2.097	1.264
H(130)	0.651	1.833	1.487
H(131)	2.938	1.701	1.129
H(132)	6.024	1.432	-2.839
H(133)	8.317	1.391	-2.147
H(134)	8.904	1.487	0.226
H(135)	7.128	1.620	1.897
H(136)	4.850	1.664	1.255
H(137)	2.278	1.578	-3.069
H(138)	-0.014	1.719	-2.710
H(139)	-1.939	1.847	-2.824
H(140)	-4.170	2.016	-3.455
H(141)	-7.901	2.370	-3.678
H(142)	-10.246	2.628	-3.264
H(143)	-11.096	2.805	-0.976
H(144)	-9.531	2.714	0.896
H(145)	-7.206	2.464	0.531
H(146)	17.252	-1.280	3.531

Table S2. The Cartesian Coordinates of the 4ANI/2CDTBT System Used for the DFT Single Point Energy Optimization in Gaussian (G09W) Package.



Atoms	X	Y	Z
N(1)	-16.165	0.615	1.633
C(2)	-17.245	0.744	0.975
C(3)	-15.141	0.403	0.911
C(4)	-18.521	0.971	1.314
C(5)	-13.844	0.213	1.190
C(6)	-16.904	0.604	-0.318
C(7)	-15.581	0.389	-0.354
C(8)	-17.812	0.684	-1.299
C(9)	-19.091	0.912	-0.956
C(10)	-19.439	1.054	0.335
C(11)	-14.729	0.186	-1.362
C(12)	-13.431	-0.003	-1.066
C(13)	-12.947	0.004	0.200
C(14)	-11.634	-0.188	0.476
C(15)	-11.052	-0.200	1.685
C(16)	-9.737	-0.412	1.579
C(17)	-9.367	-0.552	0.296
S(18)	-10.582	-0.423	-0.523
C(19)	-8.112	-0.762	-0.174
C(20)	** -7.771	-0.883	-1.476
C(21)	-7.067	-0.859	0.671
C(22)	-5.802	-1.042	0.262
C(23)	-5.448	-1.145	-1.036
C(24)	-6.493	-1.063	-1.887
N(25)	-8.612	-0.823	-2.430
N(26)	-6.365	-1.141	-3.150
S(27)	-7.859	-0.988	-3.944
C(28)	-4.157	-1.302	-1.419

SI-IIc. ^1H hfc parameters of two CTDTBT monomers with different side chains.

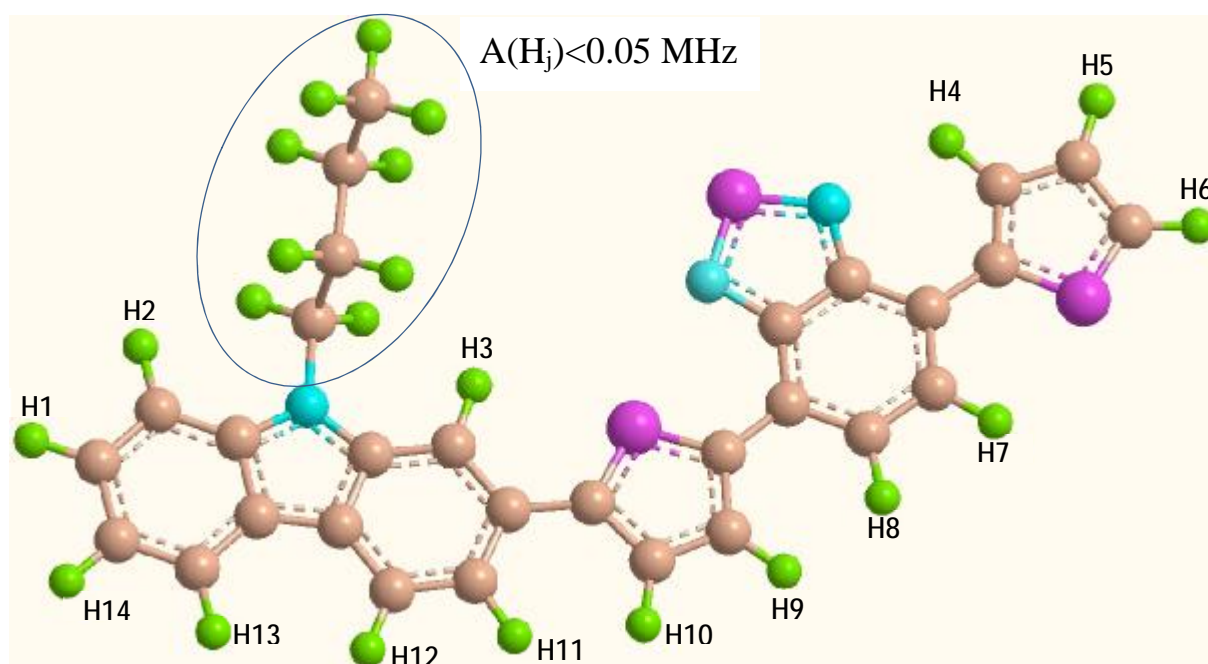


Figure S4. The CTDTBT monomer with a $-(\text{CH}_2)_3\text{-CH}_3$ side chain.

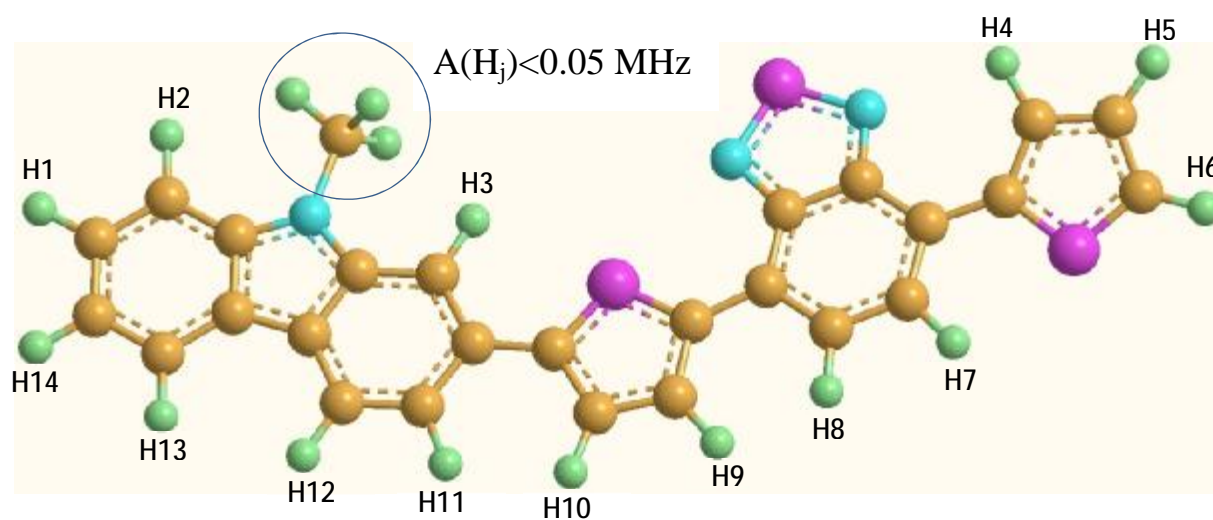


Figure S5. The CTDTBT monomer with a $(-\text{CH}_3)$ side chain.

Table S3. The hfc parameters of ^1H atoms attributed to the same positions on monomer frames.

A, MHz	H2	H3	H4	H5	H7	H8	H9	H10	H11	H12	H13	H14	N1	N2	N3
I	1.21	-3.3	-2.7	0.77	0.78	-5.7	-3.8	-2.66	-3.02	-0.44	-2.8	0.47	-1	0.04	0.7
II	1.34	-3.3	-2.8	0.74	0.3	-5.1	-4	-2.56	-3.36	-0.12	-3	0.68	-1	0.08	0.6

Note: I - $(>\text{N}-(\text{CH}_2)_3\text{-CH}_3$, II - $(>\text{N}-\text{CH}_3)$.

SI-III. Spin-Lattice Relaxation of Charge Carriers in Dual-Polymer Composite.

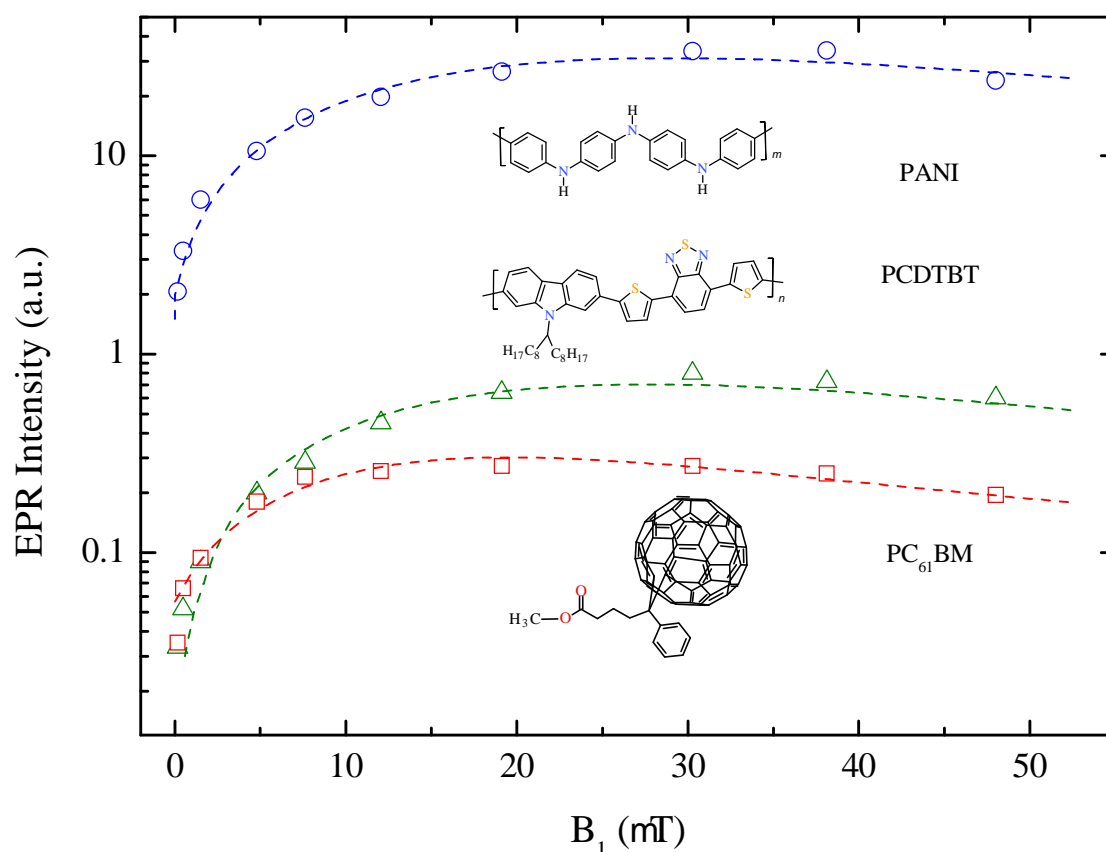


Figure S6. The intensity I of EPR lines of polarons stabilized on the PANI chains (circles), polarons initiated by photons with $h\nu_{\text{ph}}=1.97$ eV on the PCDTBT chains (triangles) as well as PC₆₁BM radical anions (squares) at $T = 77$ K as function of the magnetic term B_1 of MW field. Top-to-bottom lines calculated from equation^{S1} $I = I_0 B_1 (1 + \gamma_e^2 B_1^2 T_1 T_2)^{-3/2}$ with $T_1^{\text{PANI}}=3.2 \times 10^{-6}$ s, $T_2^{\text{PANI}}=6.1 \times 10^{-9}$ s, $T_1^{\text{P}}=1.1 \times 10^{-6}$ s, $T_2^{\text{P}}=2.1 \times 10^{-8}$ s, and $T_1^{\text{mF}}=7.7 \times 10^{-7}$ s, $T_2^{\text{mF}}=5.5 \times 10^{-8}$ s, respectively.

Reference:

(S1) Marumoto, K.; Takeuchi, N.; Ozaki, T.; Kuroda, S., ESR Studies of Photogenerated Polarons in Regioregular Poly(3-Alkylthiophene)-Fullerene Composite. *Synth. Met.* **2002**, *129*, 239-247.