Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Synergy of co-sensitizers in a copper bipyridyl redox system for efficient and cost-effective dye-sensitized solar cells in solar and ambient light

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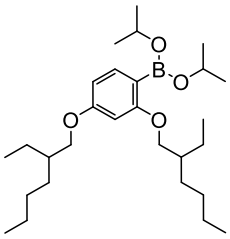
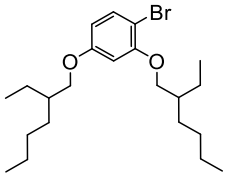
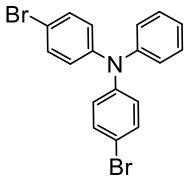
Supporting Information



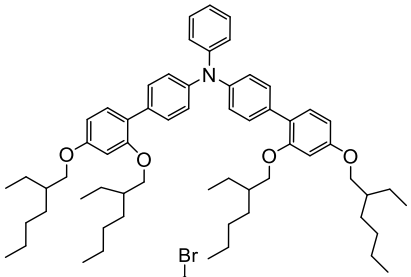
SM for Compound (1)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
4-Bromobenzene-1,3-diol	6626-15-9	0.514	14.08	$ 7.24
3-(Bromomethyl)heptane	18908-66-2	1.313	0.25	$ 0.33
Potassium carbonate anhyd.	584-08-7	1.502	0.13	$ 0.20
Dimethylformamide anhyd.	68-12-2	5.137	0.04	$ 0.19
Total				**$ 7.97**



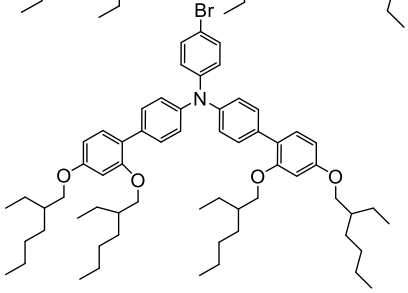
SM for Compound (2)*[1, 2]	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (1)	-	1.276	7.97	$ 10.16
Tetrahydrofuran anhyd.	109-99-9	10.804	0.09	$ 0.98
Butyl lithium (n-BuLi, 1.6M?)	109-72-8	1.417	0.09	$ 0.13
Triisopropyl borate	5419-55-6	0.637	0.23	$ 0.15
Total				**$ 11.42**



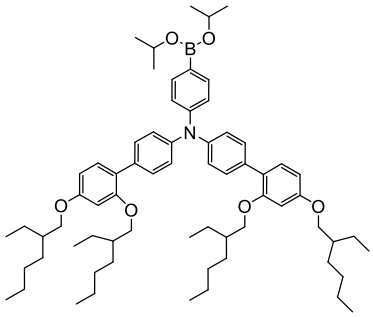
SM for Compound (3)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
N-Bromosuccinimide	128-08-5	1.187	0.08	$ 0.10
Dimethylformamide anhyd.	68-12-2	18.880	0.04	$ 0.67
Triphenylamine	603-34-9	0.816	1.48	$ 1.21
Total				**$ 1.98**



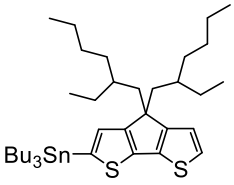
SM for Compound (4)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (2)	-	2.234	11.42	$ 25.53
Compound (3)	-	0.515	1.98	$ 1.02
Tetrahydrofuran	109-99-9	13.600	0.09	$ 1.24
$Pd(PPh_3)_4$	14221-01-3	0.00741	28.01	$ 0.21
Potassium carbonate	584-08-7	0.805	0.08	$ 0.07
Total				**$ 28.06**



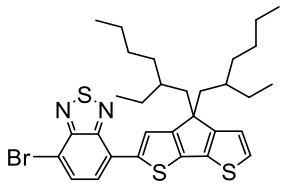
SM for Compound (5)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (4)	-	1.229	28.06	$ 34.47
N-Bromosuccinimide	128-08-5	0.257	0.08	$ 0.02
Dichloromethane	75-09-2	37.857	0.03	$ 1.11
Total				**$ 35.60**



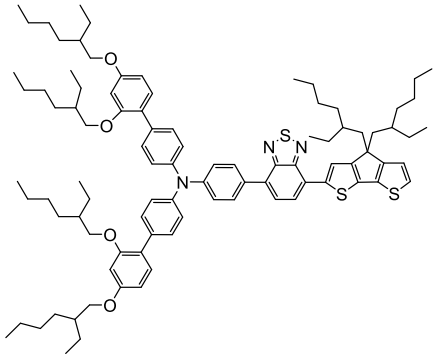
SM for Compound (6)*[1, 2]	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (5)	-	1.361	35.60	$ 48.45
Tetrahydrofuran anhyd.	109-99-9	11.679	0.09	$ 1.06
Butyl lithium (n-BuLi, 1.6 M?)	109-72-8	0.643	0.09	$ 0.06
Triisopropyl borate	5419-55-6	0.283	0.23	$ 0.06
Total				**$ 49.64**



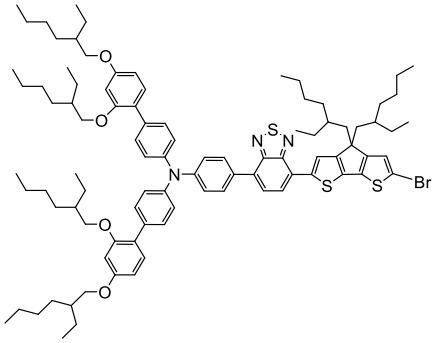
SM for Compound (7')*[3]	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
4,4-bis(2-ethylhexyl)-4H-cyclo -penta[1,2-b:5,4-b']dithiophene	365547-20-2	0.583	131.45	$ 76.59
Tetrahydrofuran anhyd.	109-99-9	4.818	0.09	$ 0.44
n-Butyllithium (2.5 M)	109-72-8	0.404	0.15	$ 0.06
Tributyltin chloride	1461-22-9	0.472	0.28	$ 0.13
Total				**$ 77.22**



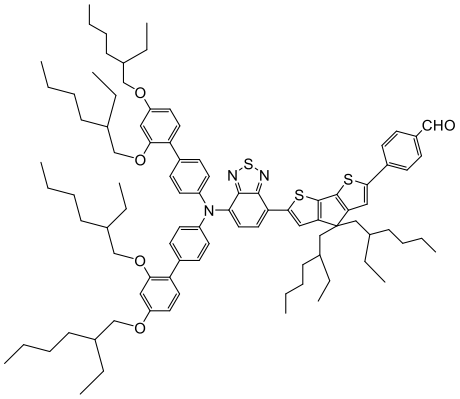
SM for Compound (7)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (7')	-	1.110	77.22	$ 85.71
4,7-dibromobenzo[c][1,2,5]thia -diazole	15155-41-6	1.973	23.24	$ 45.86
Bis(triphenylphosphine)palladi -um(II) dichloride	13965-03-2	0.106	12.22	$ 1.30
Toluene anhyd.	108-88-3	131.061	0.03	$ 4.41
Total				**$ 137.28**



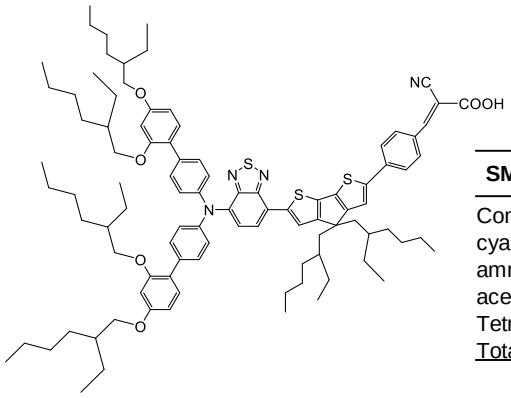
SM for Compound (8)*[4]	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (6)	-	2.093	49.64	$ 103.89
Compound (7)	-	0.745	137.28	$ 102.24
Tetrahydrofuran anhyd.	109-99-9	11.649	0.09	$ 1.06
$Pd(PPh_3)$	14221-01-3	0.00685	28.01	$ 0.19
Potassium carbonate	584-08-7	0.766	0.08	$ 0.06
Total				**$ 207.44**



SM for Compound (9)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (8)	-	1.060	207.44	$ 219.89
N-Bromosuccinimide	128-08-5	0.132	0.08	$ 0.01
Dichloromethane	75-09-2	19.433	0.03	$ 0.57
Total				**$ 220.47**



SM for Compound (10)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
4-formylphenylboronic acid	87199-17-5	0.742	15.92	$ 11.81
Compound (9)	-	1.839	220.47	$ 405.38
$Pd(PPh_3)_4$	14221-01-3	0.323	28.01	$ 9.03
Potassium carbonate anhyd.	584-08-7	6.452	0.13	$ 0.85
Tetrahydrofuran anhyd.	109-99-9	286.774	0.09	$ 26.06
Total				**$ 453.14**



SM for XY1	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (10)	-	1.116	453.14	$ 505.66
cyanoacetic acid	372-09-8	27.468	0.13	$ 3.66
ammonium acetate	631-61-8	29.185	0.10	$ 2.85
acetic acid	64-19-7	540.258	0.04	$ 24.20
Tetrahydrofuran anhyd.	109-99-9	7.631	0.09	$ 0.69
Total				**$ 537.063**

Fig S1 Step-by-step cost calculation of XY1. The molecular structure of the intermediate (or final) product of each step is presented along with the simplified cost of synthesis. The compound numbers are associated to the original literature.[1] The total cost of starting materials to obtain 1g of product was calculated for each step, with the yield of the product taken into account. SM: starting material; G_S: 1 g of starting material; G_P: 1 g of product. The cost of each reagent was searched from https://www.sigmaaldrich.com/united-kingdom.html (accessed 20 June 2019), where the least expensive available product was selected. All costs were converted from GBP to USD using a conversion rate of 1GBP = 1.28 USD.

*1 Since the yield is not indicated in the literature for Compounds (2) and (6), we assumed it as 70% in this study.

*2 Butyl lithium was assumed as n-BuLi, 1.6 M for Compounds (2) and (6).

*3 4,4-bis(2-ethylhexyl)-4H-cyclopenta[1,2-b:5,4-b']dithiophen-2-yl)tributylstannane, one of the starting materials for Compound (7) does not appear on the Sigma Aldrich website or elsewhere according to our search. Therefore, the cost of this reagent (Compound (7')) was determined by calculating the synthesis cost of a literature procedure (DOI: 10.1039/b901374a).[2]

*4 For the synthesis of Compound (8), we made the following assumptions for the amount of reagents to obtain 1 g of product: 0.50 mmol of Compound (6) (in 0.25 mL THF), 0.30 mmol of Compound (7), 3.25 mL of THF in total (0.25 mL + 3.0 mL), 1.7 mg of $Pd(PPh_3)_4$ and 0.19 g of KI.

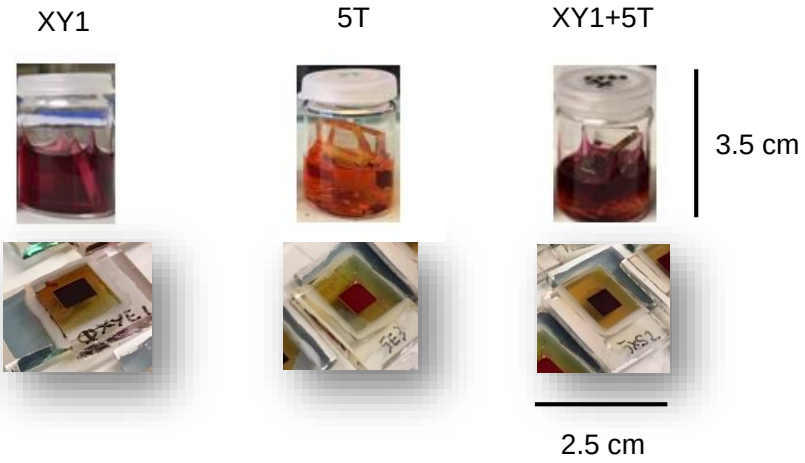


Fig. S2 Top: photographs of the dye baths (scale bar = 3.5 cm); 5T (left), XY1 (middle) and XY1+5T (right). Bottom: The corresponding devices (scale bar = 2.5 cm).

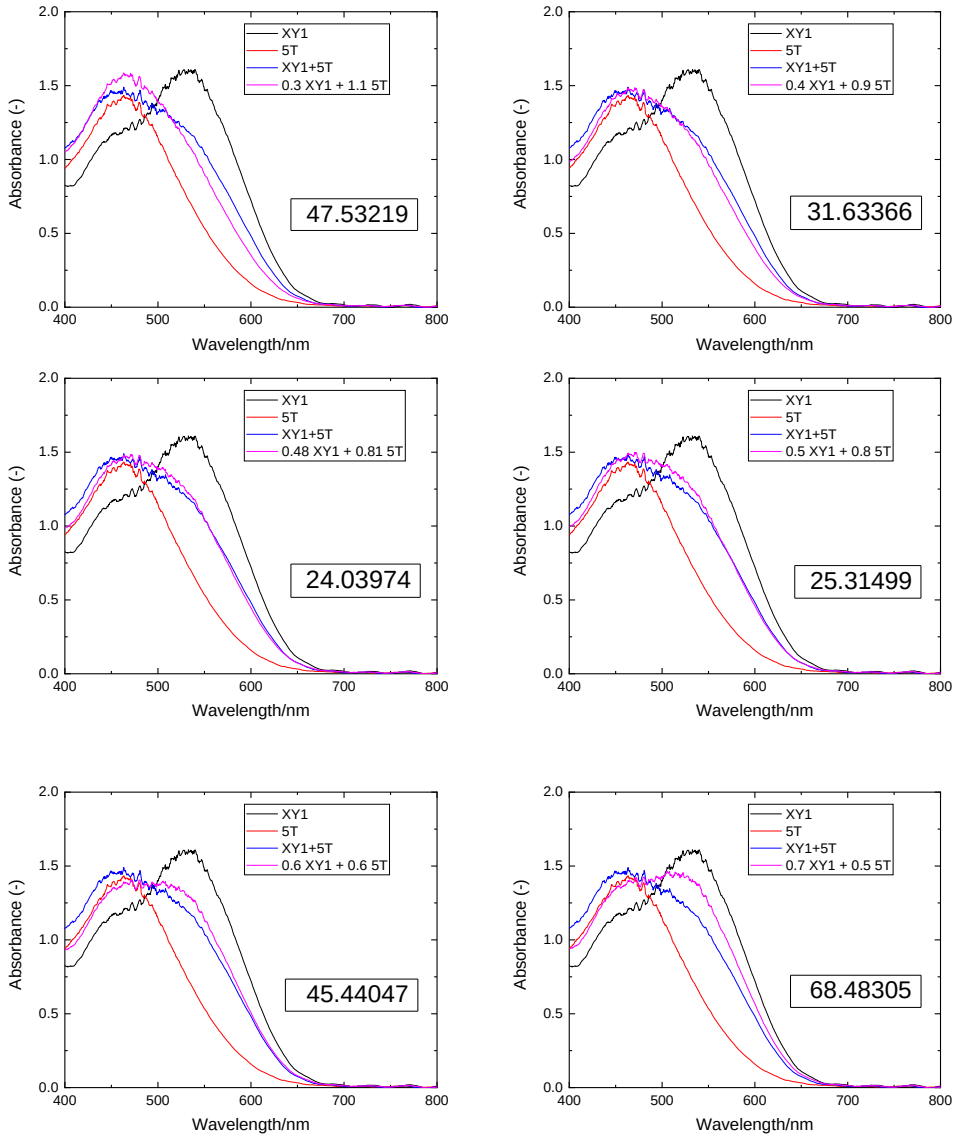


Fig. S3 Different fitting trials of the XY1+5T UV-Vis spectra. The value in the box signifies the total error of the absorbance between the actual XY1+5T spectra and simulated XY1 + 5T spectra in the wavelength range of 400-800 nm.

The peak absorbance in the solid-state UV-Vis spectra was taken and the dye ratio in XY1- and 5T- only samples was calculated based on the liquid-state UV-Vis absorption spectra. The molecular extinction coefficient of XY1 dye and 5T dye in liquid state is 56500 M^{-1} cm^{-1} at 552 nm 39000 M^{-1} cm^{-1} at 478 nm, respectively (1:0.690). The peak absorbance ratio of XY1 and 5T in solid-state is 1:0.890, thus the molar ratio of each dye in the sensitized film is calculated as 1:1.29. In other words, the XY1-only film contains 1 XY1 and the 5T-only film contains 1.29 5T. Based on these results, integration of different ratios of XY1 and 5T were fitted to the measured absorption spectra of XY1+5T. The error between (a XY1 + b 5T) (where a and b describe the molar equivalent of XY1 dye and 5T dye) and XY1+5T was compared by integrating the y-axis difference over the wavelength from 400-800 nm. At first, the amount of 5T dye down to the first decimal with minimal error was searched for fixed XY1 dye values at 0.3-0.7. Then the optimal amount of 5T dye with 2 decimals was searched for XY1 dye values at 0.47-0.50, to find the best ratio of XY1/5T with minimal error.

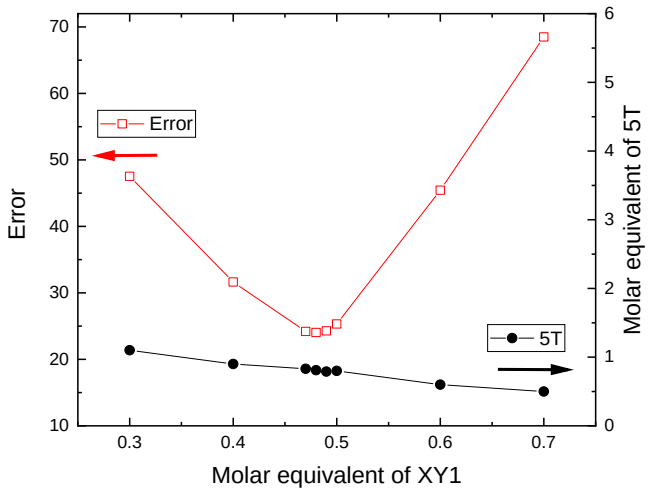


Fig. S4 Relation between the molar equivalent of XY1 dye (and 5T dye) and the error between XY1+5T and fitted XY1 + 5T spectra in Fig. S3.

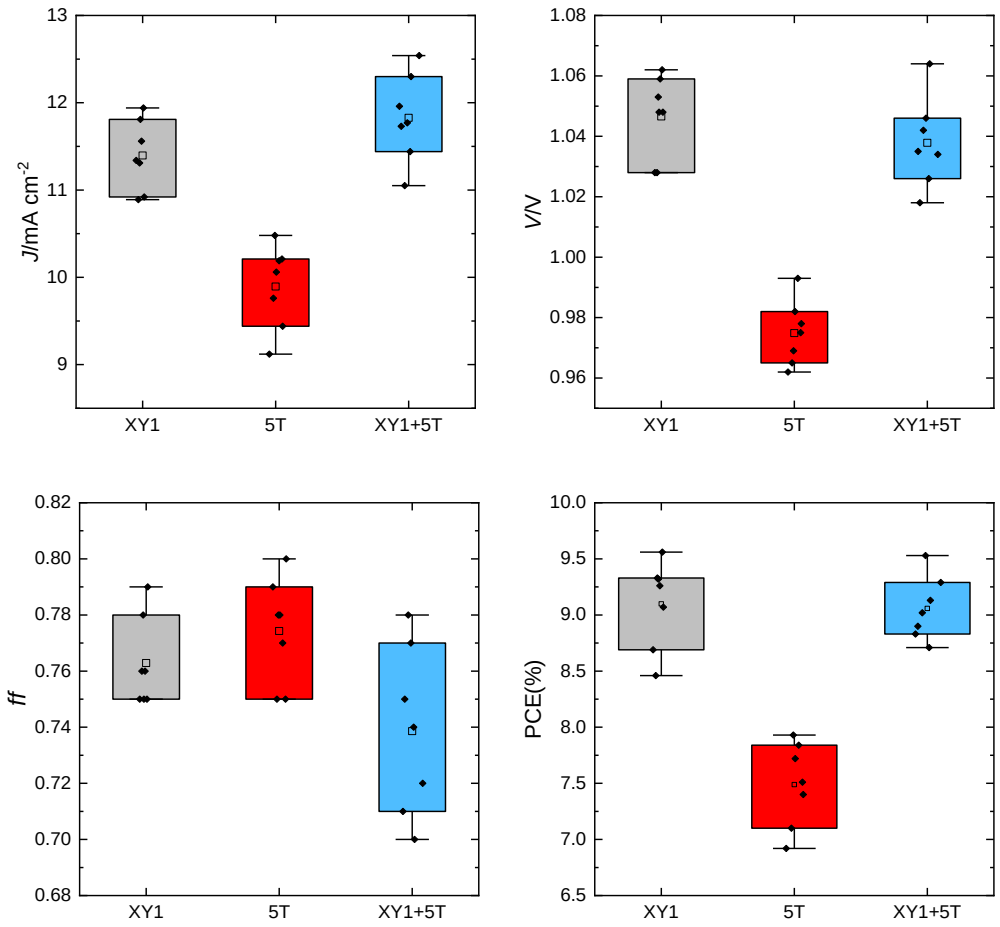


Fig. S5 Statistical performance of the DSSCs with XY1, 5T and XY1+5T, illuminated at 1 sun. 7 cells were repeated for each condition. Dots: data points; square: mean; box: 25-75% range; whiskers: 1.5 interquartile range.

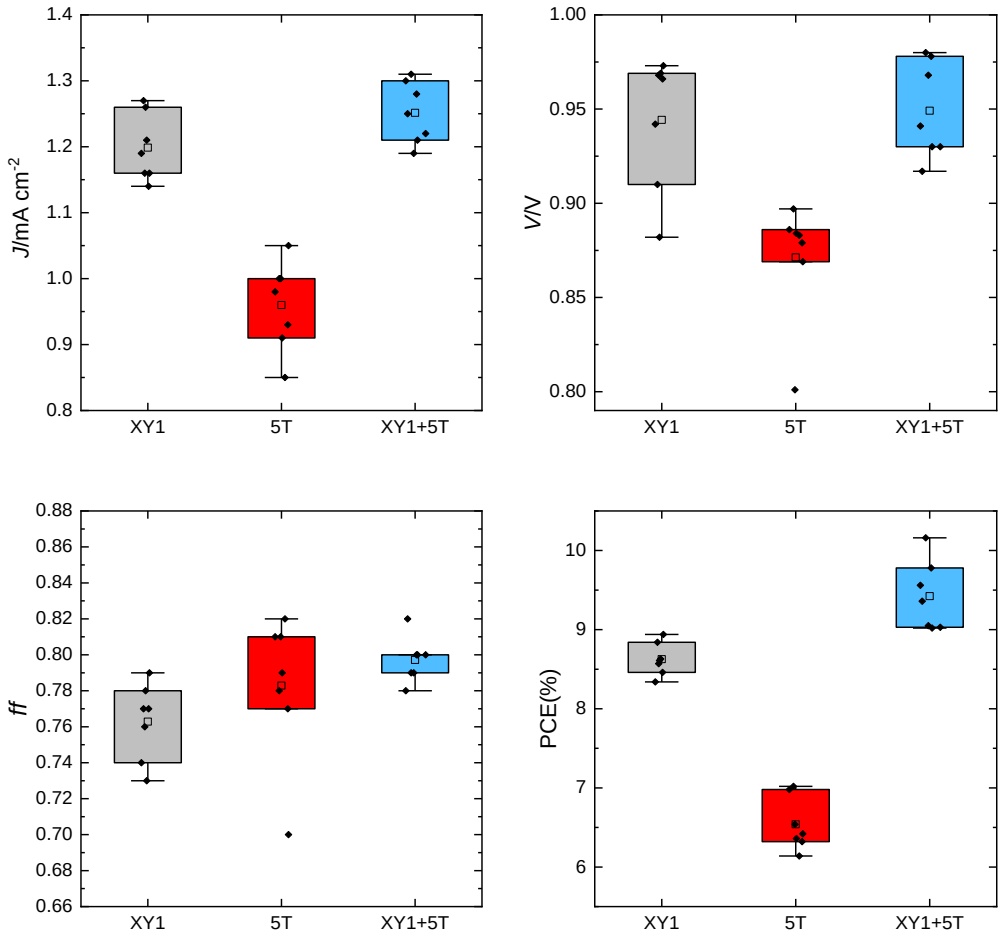


Fig. S6 Statistical performance of the DSSCs with XY1, 5T and XY1+5T, illuminated at 0.1 sun. 7 cells were repeated for each condition. Dots: data points; square: mean; box: 25-75% range; whiskers: 1.5 interquartile range.

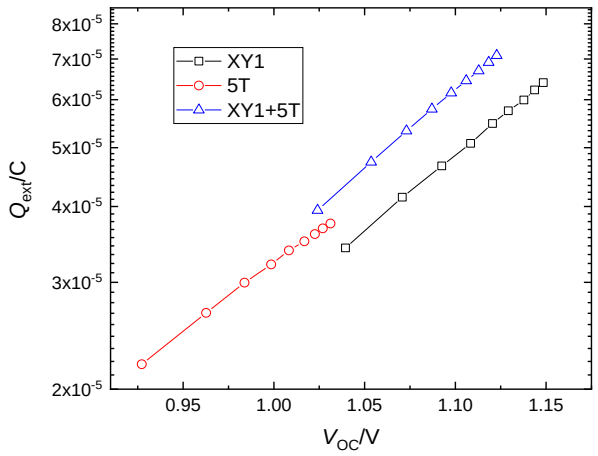


Fig. S7 Charge extraction curves of the best DSSCs (XY1, 5T and XY1+5T) at V_{OC}.

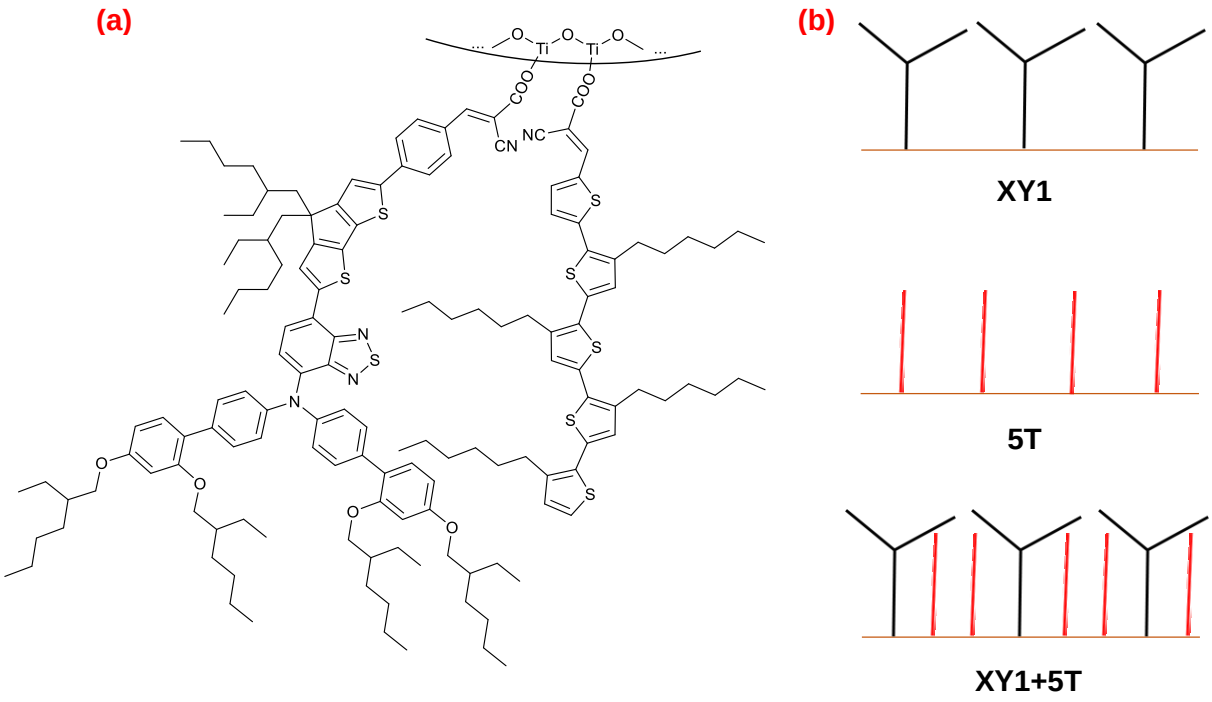


Fig. S8 (a) Descriptive molecular image of the binding of XY1 dye and 5T dye to the TiO_2 nanoparticles in XY1+5T, and (b) a simplified illustration of the dyes bound in the case of XY1, 5T and XY1+5T. Black Y-shape: XY1 dye; red I-shape: 5T dye; brown line: TiO_2 surface.

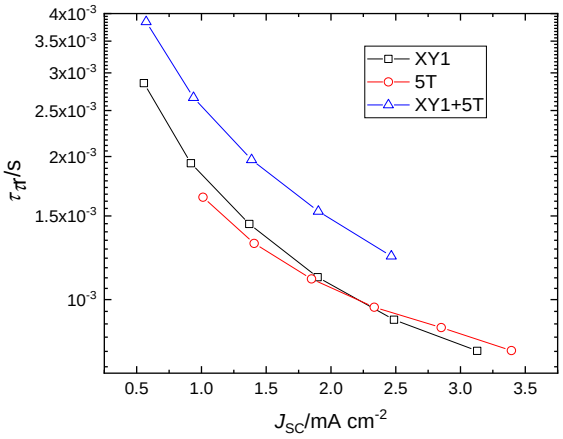


Fig. S9 Charge transport curves of the best DSSCs (XY1, 5T and XY1+5T) at J_{SC}.

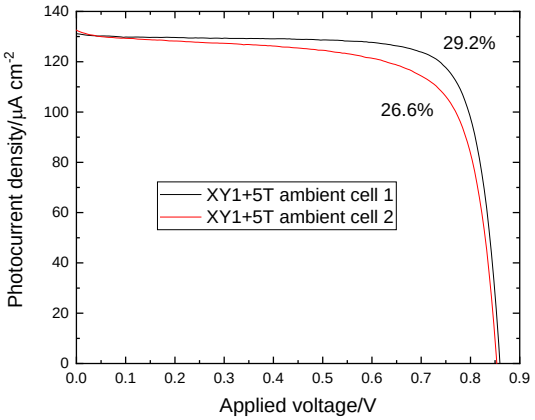
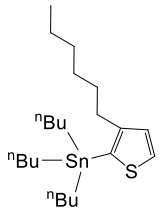


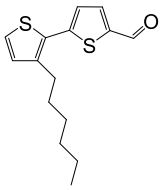
Fig. S10 *J-V* curves of XY1+5T-sensitized DSSCs tested under 1000 lux warm fluorescent light. Two cells were fabricated with the same condition.

Table 1 Statistical performance of the two XY1+5T-sensitized DSSCs tested under 1000 lux warm fluorescent light.

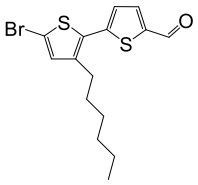
Cell no.	J_{SC}/μA cm^{-2}	V_{OC}/V	*ff*	P_{in}/μW cm^{-2}	P_{out}/μW cm^{-2}	PCE(%)
1	131.2	0.860	0.78	303.1	88.5	29.2
2	132.7	0.853	0.71	303.1	80.6	26.6
Avg.	132 ± 1	0.857 ± 0.005	0.75 ±0.05	303.1	85±6	28±2



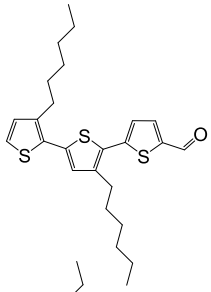
SM for Compound (2)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Mg turnings	7439-95-4	0.058	0.24	$ 0.01
Tetrahydrofuran anhyd.	109-99-9	1.954	0.09	$ 0.18
2-bromo-3-hexylthiophene	69249-61-2	0.550	29.18	$ 16.04
Tributyltinchloride	1461-22-9	0.791	0.28	$ 0.22
Total				**$ 16.45**



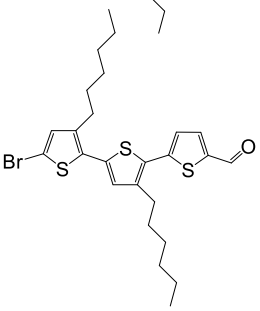
SM for Compound (3)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Tri(o-tolyl)phosphine	6163-58-2	0.0950	17.28	$ 1.64
Tris(dibenzylideneacetone)dip-alladium	51364-51-3	0.143	15.72	$ 2.25
5-bromo-2-thiophenecarbox-aldehyde	4701-17-1	0.997	2.34	$ 2.33
Compound (2)	-	2.392	16.45	$ 39.35
Toluene anhyd.	108-88-3	18.105	0.03	$ 0.61
Potassium fluoride	7789-23-3	1.351	0.35	$ 0.47
Total				**$ 46.65**



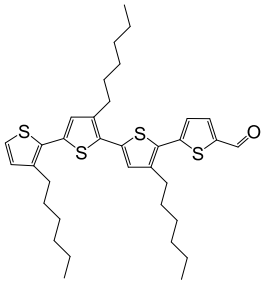
SM for Compound (4)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (3)	-	1.261	46.65	$ 58.81
Dimethylformamide anhyd.	68-12-2	13.089	0.04	$ 0.47
N-Bromosuccinimide	128-08-5	0.958	0.08	$ 0.08
Total				**$ 59.35**



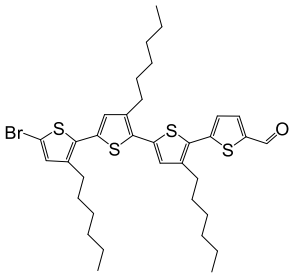
SM for Compound (5)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Tri(o-tolyl)phosphine	6163-58-2	0.060	17.28	$ 1.04
Tris(dibenzylideneacetone)dip-alladium	51364-51-3	0.0910	15.72	$ 1.43
Compound (4)	-	1.184	59.35	$ 70.28
Compound (2)	-	1.771	16.45	$ 29.13
Toluene anhyd.	108-88-3	10.759	0.03	$ 0.36
Potassium fluoride	7789-23-3	0.723	0.35	$ 0.25
Total				**$ 102.50**



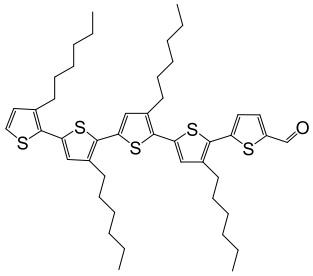
SM for Compound (6)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (5)	-	1.000	102.50	$ 102.50
Dimethylformamide anhyd.	68-12-2	6.608	0.04	$ 0.24
N-Bromosuccinimide	128-08-5	0.400	0.08	$ 0.03
Total				**$ 102.76**



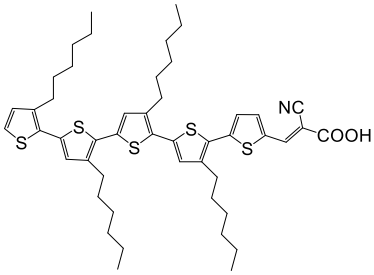
SM for Compound (7)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Tri(o-tolyl)phosphine	6163-58-2	0.0416	17.28	$ 0.72
Tris(dibenzylideneacetone)dip-alladium	51364-51-3	0.0633	15.72	$ 0.99
Compound (6)	-	1.205	102.76	$ 123.81
Compound (2)	-	1.157	16.45	$ 19.03
Toluene anhyd.	108-88-3	7.816	0.03	$ 0.26
Potassium fluoride	7789-23-3	0.350	0.35	$ 0.12
Total				**$ 144.94**



SM for Compound (8)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (7)	-	0.962	144.94	$ 139.36
Dimethylformamide anhyd.	68-12-2	7.262	0.04	$ 0.26
N-Bromosuccinimide	128-08-5	0.280	0.08	$ 0.02
Total				**$ 139.64**



SM for Compound (9)	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Tri(o-tolyl)phosphine	6163-58-2	0.0336	17.28	$ 0.58
Tris(dibenzylideneacetone)dip-alladium	51364-51-3	0.0492	15.72	$ 0.77
Compound (8)	-	1.249	139.64	$ 174.35
Compound (2)	-	0.912	16.45	$ 15.01
Toluene anhyd.	108-88-3	6.231	0.03	$ 0.21
Potassium fluoride	7789-23-3	0.698	0.35	$ 0.24
Total				**$ 191.16**



SM for 5T	CAS	SM [g]/G_p	SM [$]/$G_s$	SM [$]/$G_p$
Compound (9)	-	1.695	191.16	$ 324.00
Cyanoacetic acid	372-09-8	0.280	0.13	$ 0.04
Ethanol anhyd.	64-17-5	13.373	0.08	$ 1.12
Piperidine	110-89-4	0.949	0.28	$ 0.26
Total				**$ 325.426**

Fig. S11 Step-by-step cost calculation of 5T. The molecular structure of the intermediate (or final) product of each step is presented along with the simplified cost of synthesis. The compound numbers are associated with the original literature.[3] The total cost of starting materials to obtain 1g of product was calculated for each step, with the yield of the product taken into account. SM: starting material; G_S: 1 g of starting material; G_P: 1 g of product. The cost of each reagent was searched from https://www.sigmaaldrich.com/united-kingdom.html (accessed 20 June 2019), where the least expensive available product was selected. All costs were converted from GBP to USD using a conversion rate of 1GBP = 1.28 USD.

Table S2 Summary of the calculated costs of the dyes.

Dye	Cost/g	Cost/mmol[*1]	Mol eq./cm^{-2}	Cost/cm^{-2}[*2]	Cost eq./PCE[*3]
XY1	$537.06	$868.10 (1.00)	1.00	$0.022 (1.00)	1.00 (1.00)
5T	$325.43	$275.09 (0.32)	1.29	$0.009 (0.41)	0.50 (0.54)
XY1+5T	$437.85	$495.75 (0.57)	0.48 + 0.81	$0.016 (0.74)	0.74 (0.68)

*1 The values in brackets are the relative costs.

*2 The values in brackets are the relative costs. The dye coverage of XY1 was assumed as 2.5 10^{-8} mol cm^{-2}.

*3 The values in brackets are the values at 0.1 sun.

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