Supporting Information for

A new sensitizer containing dihexyloxy-substituted triphenylamine as donor and a binary conjugated spacer for dye-sensitized solar cells

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Starting materials

All reactions were carried out under nitrogen atmosphere. *p*-iodophenol 99%, 1-bromohexane 98%, 4-bromoaniline 99% (GC), 1,10-phenanthroline 99%, 5-formyl-2-furanboronic acid, 3-hexylthiophene 99%, cyanoacetic acid 99%, silica gel 60 for column chromatography (0.063-0.2 mm), *n*-butyl lithium, 2.5 M solution in hexane, tetrakis(triphenylphosphine)palladium(0), 99%, potassium *t*-butoxide 95%, potassium carbonate granulated (puriss. 99-101 %), sodium hydroxide pellets (puriss., ACS reagent), sodium sulfate anhydrous (puriss., 99-100.5%), sodium hydrogen carbonate powder (extra pure), potassium hydroxide pellets (puriss., 99-100.5%), copper(I) chloride (puriss, ACS reagent, 97%), $POCl_3$ (99%), hydrochloric acid (min. 37 %), anhydrous N,N-dimethylformamide 99.8%, dichloromethane (DCM) R.G (reagent ACS, stabilized with amylene), toluene (reagent ACS), hexane (mixture of isomers), ethyl acetate (extra pure), anhydrous tetrahydrofuran ($\geq$ 99.9%), ethanol 96% (puriss. p.a.), diethylether (reagent ACS), 1,2-dichloroethane 99+% (ACS reagent), chloroform (for HPLC, $\geq$99.9%), methanol (puriss, ACS reagent, 99.8%) were purchased from Sigma-Aldrich. Copper (I) iodide Puratronic 99.998% (metals basis) and diethyl iodomethylphosphonate 98+% were purchased from Alfa Aesar, while piperidine 99.5 % was acquired from Acros Organics. All the chemicals and solvents used in this work were analytical grade and used without further purification.

Reaction mechanism

A novel dihexyloxy-substituted triphenylamine-based dye, named *3-{5-[2-(5-{4-[bis(4-hexyloxy-phenyl)-amino]-phenyl}-furan-2-yl)-vinyl]-3-hexyl-thiophen-2-yl}-2-cyano-acrylic acid* (**BCS-1**), previously designed[20], was synthesized by a 9-step reaction sequence as shown in Scheme 1. Organometallic Suzuki coupling reaction of 4-bromo-*N,N*-bis(4-(hexyloxy)phenyl) aniline (***1***), previously obtained from 1-(hexyloxy)-4-iodobenzene and

4-bromoaniline, with 5-formyl-2-furanboronic acid was employed in order to introduce the furan ring into the conjugated linker of the dye, resulting in 5-(4-(bis(4-(hexyloxy)phenyl)amino)phenyl)furan-2-carbaldehyde (***2***). The full, binary π-conjugated spacer was achieved through the formation of the vinyl linkage between furan and thiophene moieties, by the reaction of ***2*** with diethyl [(3-hexylthiophen-2-yl)methyl]phosphonate to form *N,N*-(bis(4-hexyloxy-phenyl)-*N*-(4-(5-(2-(3-hexylthiophen-2-yl)vinyl)furan-2-yl)phenyl-aniline ***(3)***. The formylation of ***3*** through the Vilsmeier reaction afforded the corresponding aldehyde (***4***) that underwent Knoevenagel condensation with cyanoacetic acid to yield the envisaged dye, **BCS-1**.

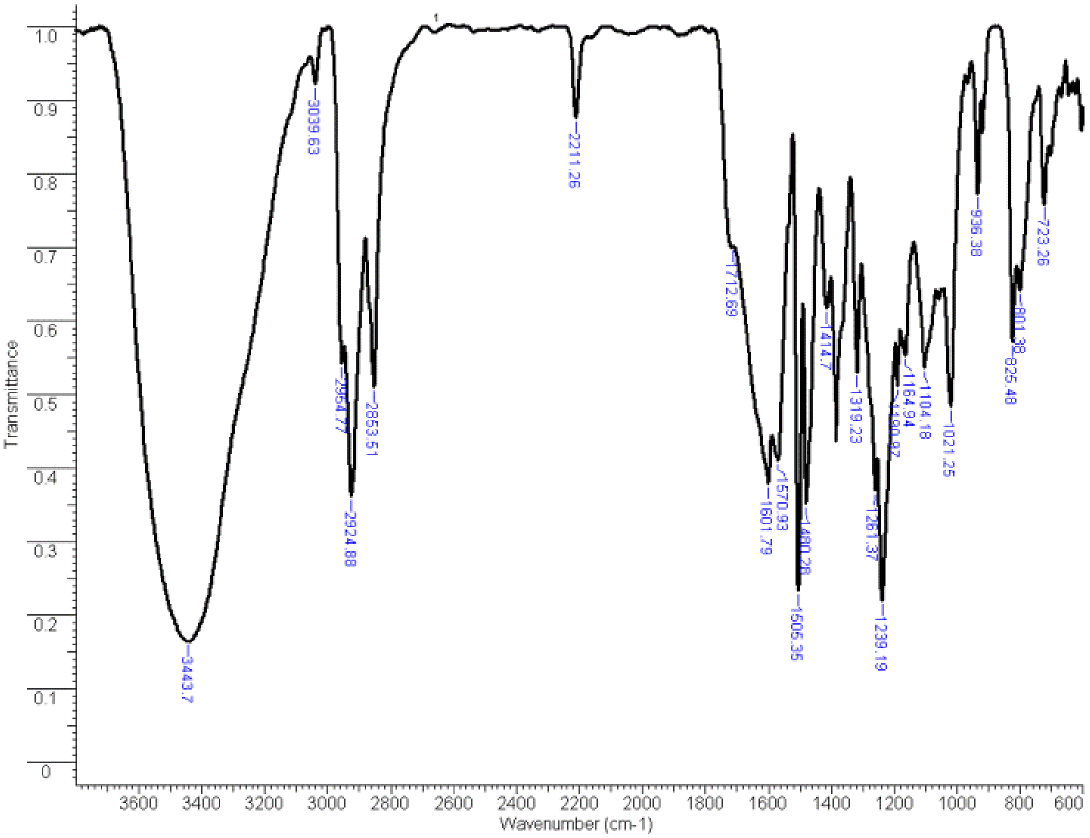

Figure S1. FTIR spectrum of **BCS-1** dye

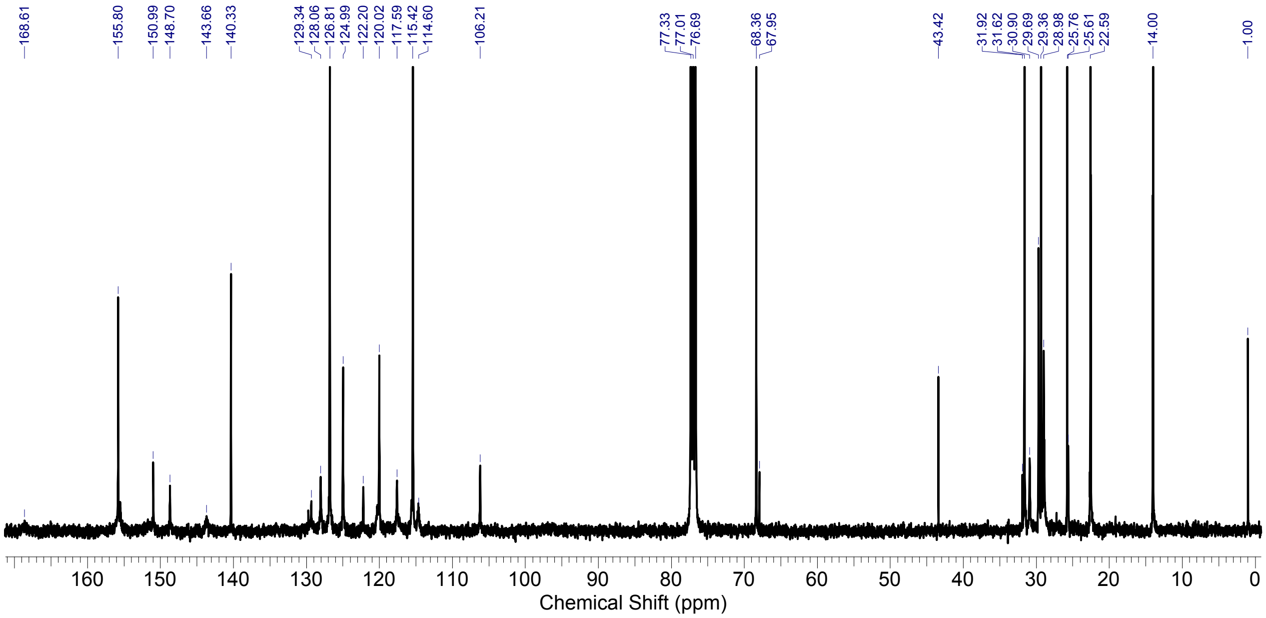

Figure S2. ^{13}C-NMR spectrum of **BCS-1** dye

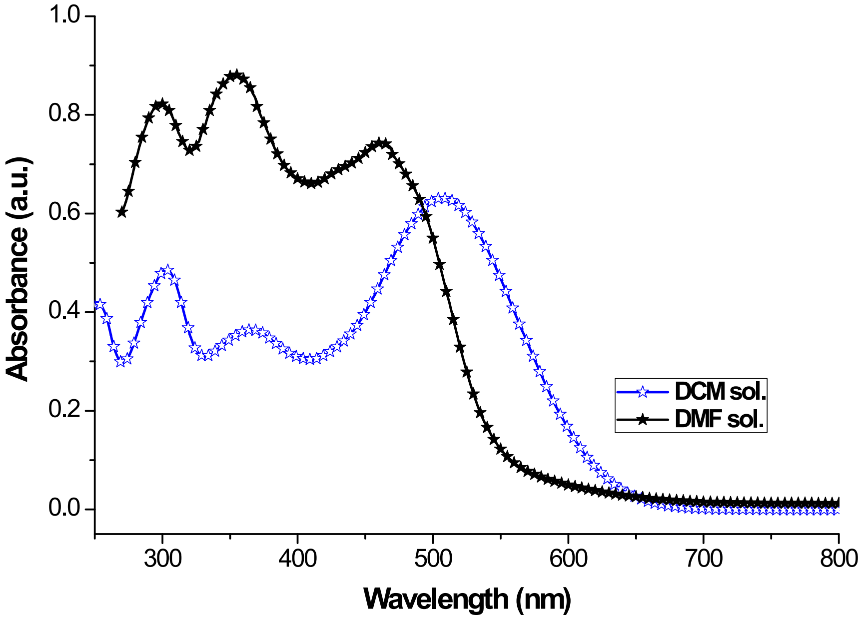

Figure S3. UV-Vis absorption spectra of **BCS-1** dye in different solvents

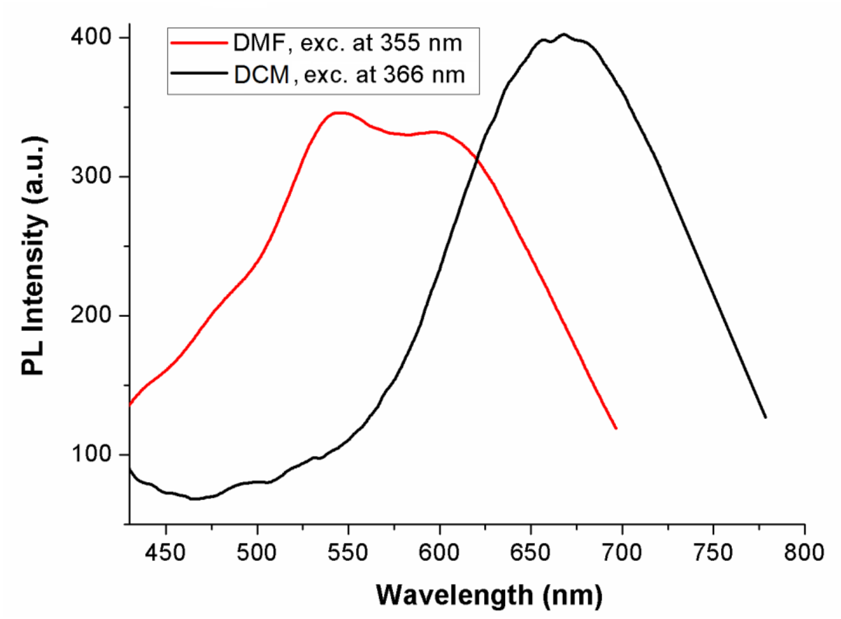

Figure S4. Photoluminescence spectra of **BCS-1** dye in different solvents by excitation at approx. 360 nm

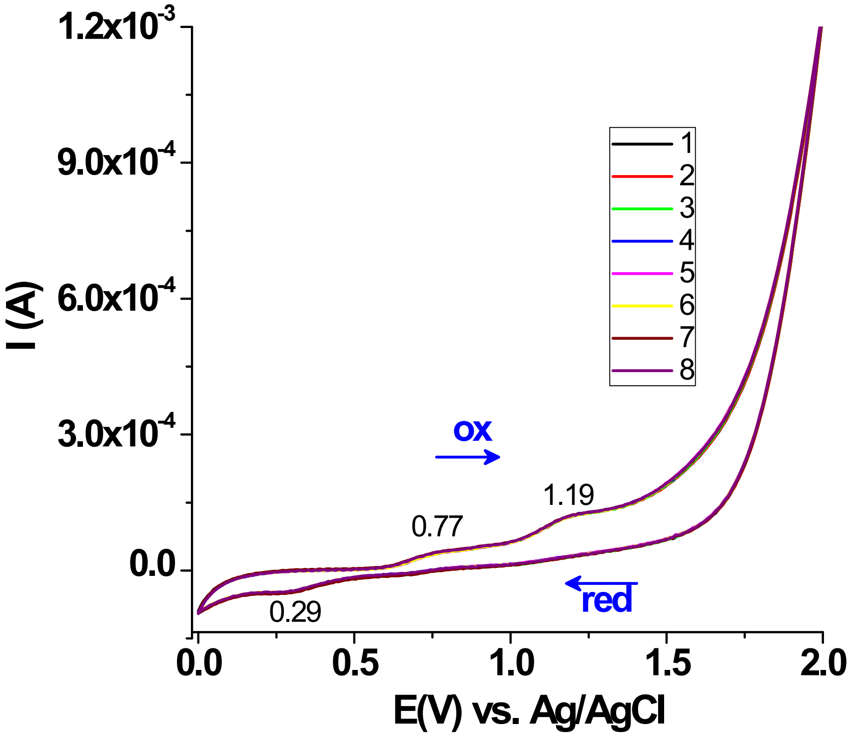

Figure S5. Cyclic voltammograms of **BCS-1** in TBAP/DMF solution (8 consecutive scans)

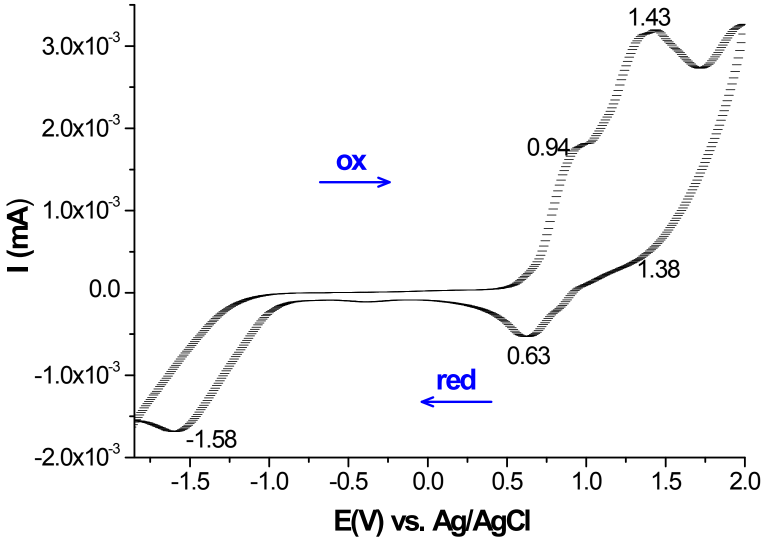

Figure S6. Cyclic voltammogram of **BCS-1** in solid state recorded at 50 mV/s

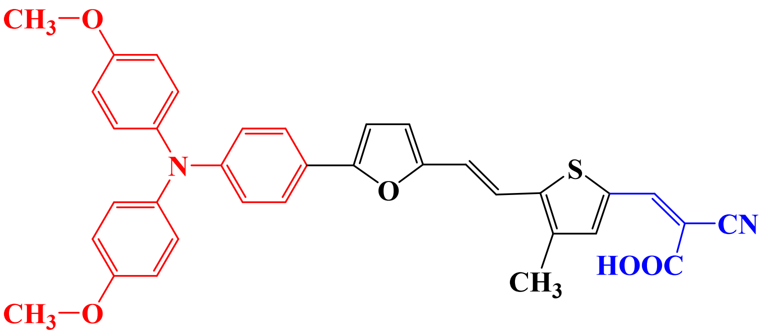

Figure S7. Molecular structure of **BCS-1m**, the model of the **BCS-1** dye used for electronic structure calculations

Computational details

The Gaussian09 input used for geometry optimization at the B3LYP/311++G** level, using the geometry optimized at B3LYP/31+G* level as starting geometry.

```
#p opt=calcall  b3lyp/6-311++G**  guess=read
scf=tight int=(grid=99974) pop=regular
```

The total energy obtained is:

```
E(RB3LYP) =  -2234.85859252     A.U. after    9 cycles
Convg  =    0.8234D-08              -V/T =  2.0037
```

The geometry convergence criteria attained are:

```
        Item               Value     Threshold  Converged?
 Maximum Force            0.000005     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
 Maximum Displacement     0.000905     0.001800     YES
 RMS     Displacement     0.000176     0.001200     YES
```

The optimized geometry is listed below:

```
C       6.202974    3.480851    0.888687
C       5.970023    2.117235    0.966313
C       5.267919    1.450843   -0.048593
C       4.806691    2.190967   -1.137318
C       5.019186    3.568057   -1.214466
C       5.724671    4.220554   -0.200272
H       6.745273    3.999037    1.670390
H       6.338055    1.555295    1.816539
H       4.268626    1.690368   -1.933705
H       4.643682    4.109589   -2.072265
N       5.050259    0.041462    0.028591
C       6.171634   -0.804257    0.286077
C       6.117673   -1.780861    1.292319
C       7.353805   -0.659267   -0.439220
C       7.209247   -2.594070    1.549034
H       5.210090   -1.899935    1.872293
C       8.465393   -1.460673   -0.173961
H       7.414029    0.094405   -1.215391
C       8.395509   -2.439617    0.819685
H       7.171469   -3.348869    2.325289
H       9.366758   -1.315937   -0.754137
C       3.770063   -0.500436   -0.163829
C       2.613502    0.230956    0.165756
C       3.601172   -1.795361   -0.692429
C       1.351589   -0.306415   -0.026820
H       2.712094    1.225680    0.581028
C       2.337350   -2.328396   -0.875743
H       4.471264   -2.378814   -0.964318
C       1.179211   -1.600096   -0.549837
H       0.480920    0.276740    0.245238
H       2.249580   -3.324172   -1.294927
C      -0.137639   -2.168498   -0.747468
C      -0.580429   -3.394404   -1.197931
C      -1.993246   -3.357816   -1.169306
C      -2.356964   -2.112640   -0.701635
H      -2.674886   -4.144436   -1.453269
C      -3.630946   -1.526061   -0.468872
C      -3.852811   -0.270207    0.004529
H      -4.469394   -2.175398   -0.703589
H      -2.993147    0.351398    0.230239
C      -5.131807    0.329363    0.241656
C      -5.355367    1.621920    0.735862
S      -6.635635   -0.506587   -0.067120
C      -6.721622    1.907697    0.854462
C      -7.576661    0.877613    0.467540
H      -7.103707    2.854221    1.218424
C      -8.988994    0.967543    0.511425
C      -9.968318    0.068730    0.175019
H      -9.369543    1.918050    0.876707
```

```
C     -11.374784    0.497882    0.348205
O     -11.724585    1.581048    0.763557
O     -12.256261   -0.463073   -0.012223
H     -13.142606   -0.101072    0.132020
O       9.415265   -3.282191    1.155456
O       5.997066    5.557784   -0.178589
C       5.540343    6.361913   -1.257697
H       4.448098    6.338846   -1.339357
H       5.862839    7.376475   -1.029906
H       5.984197    6.045752   -2.208030
C      10.644876   -3.174920    0.450937
H      11.097027   -2.185979    0.584038
H      11.300323   -3.931036    0.879773
H      10.512046   -3.374841   -0.617931
C      -9.698221   -1.233612   -0.323966
N      -9.460658   -2.291546   -0.729591
H       0.038518   -4.220620   -1.507363
C      -4.259166    2.587931    1.097339
H      -3.613652    2.189617    1.885962
H      -3.623385    2.817786    0.236956
H      -4.680647    3.527708    1.457861
O      -1.218498   -1.387140   -0.444521
```

The Gaussian09 route used for computing the excited states energies and oscillator strengths of BCS-1m using time-dependent CAM-B3LYP with the 6-311++G** basis set is listed below.

```
#p td=(50-50,nstates=10) cam-b3lyp/6-311++G**
geom=check guess=read scf=tight int=(grid=99974) pop=regular
```

The total energy obtained is:

```
E(RCAM-B3LYP) =  -2233.90031102     A.U. after   18 cycles
  Convg  =    0.7194D-08             -V/T =  2.0035
```

The excited states energies, wavelengths, and oscillator strengths are listed below:

```
  1: Triplet  0.9478 eV 1308.18 nm  f=0.0000  <S**2>=2.000
  2: Triplet  2.0674 eV  599.71 nm  f=0.0000  <S**2>=2.000
  3: Singlet  2.4436 eV  507.38 nm  f=1.6059  <S**2>=0.000
  4: Triplet  2.7459 eV  451.52 nm  f=0.0000  <S**2>=2.000
  5: Triplet  3.1253 eV  396.71 nm  f=0.0000  <S**2>=2.000
  6: Triplet  3.2334 eV  383.45 nm  f=0.0000  <S**2>=2.000
  7: Triplet  3.2656 eV  379.67 nm  f=0.0000  <S**2>=2.000
  8: Triplet  3.3077 eV  374.83 nm  f=0.0000  <S**2>=2.000
  9: Triplet  3.4302 eV  361.44 nm  f=0.0000  <S**2>=2.000
 10: Singlet  3.4411 eV  360.31 nm  f=0.0302  <S**2>=0.000
 11: Triplet  3.5917 eV  345.19 nm  f=0.0000  <S**2>=2.000
 12: Singlet  3.7548 eV  330.20 nm  f=0.2102  <S**2>=0.000
 13: Triplet  3.8029 eV  326.03 nm  f=0.0000  <S**2>=2.000
 14: Singlet  3.8231 eV  324.30 nm  f=0.0195  <S**2>=0.000
 15: Singlet  3.9013 eV  317.80 nm  f=0.0462  <S**2>=0.000
 16: Singlet  4.0958 eV  302.71 nm  f=0.0529  <S**2>=0.000
 17: Singlet  4.2245 eV  293.49 nm  f=0.1790  <S**2>=0.000
 18: Singlet  4.3115 eV  287.56 nm  f=0.1601  <S**2>=0.000
 19: Singlet  4.4227 eV  280.34 nm  f=0.0753  <S**2>=0.000
 20: Singlet  4.4493 eV  278.66 nm  f=0.0771  <S**2>=0.000
```

The isotropic polarizability was computed at the B3LYP/6-311++G** level using the Gaussian09 route below using the geometry optimized at the same theory level.

```
#p  polar  b3lyp/6-311++G**  geom=check  guess=read  int=(grid=99974)
```

The obtained isotropic polarizability:

```
SCF Polarizability for W=    0.000000:
                1             2             3
      1  0.135561D+04
      2 -0.613112D+02  0.549734D+03
      3 -0.148733D+02  0.357017D+02  0.304231D+03
 Isotropic polarizability for W=    0.000000      736.53 Bohr**3.
```