

Supporting Information

Thiophenol detection using an AIE fluorescent probe through self-assembly with TPE-based glycoclusters

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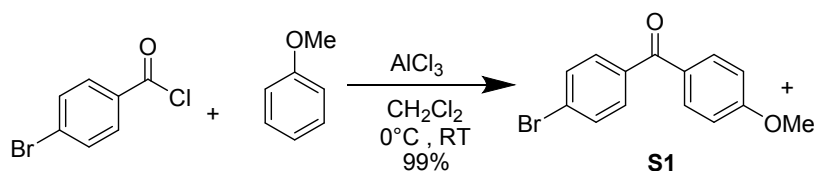
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Contents List

Synthesis of the TD-based probes and TPE-based glycoclusters	S1-S19
Experimental section for fluorescence measurement	S20
Additional figures and schemes	S21-S25
References	S26

General methods

All reagents for synthesis commercially available (highest purity available for reagent grade compounds) were used without further purification. Reactions under microwave activation were performed on a Biotage Initiator system. Thin-layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 F₂₅₄ (Merck). TLC plates were inspected by UV light ($\lambda = 254 \text{ nm}, 365 \text{ nm}$) and developed by treatment with a mixture of 10% H₂SO₄ in EtOH/H₂O (95:5 v/v) followed by heating. Silica gel column chromatography was performed with silica gel Si 60 (40–63 μm). NMR spectra were recorded at 293 K, unless stated otherwise. Chemical shifts are referenced relative to deuterated solvent residual peaks. The following abbreviations are used to explain the observed multiplicities: s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet; p, pseudo and b, broad. Complete signal assignments were based on 1D and 2D NMR correlations COSY and HSQC. High resolution (HR-ESI-QToF) mass spectra were recorded using a Bruker MicroToF-Q II XL spectrometer.



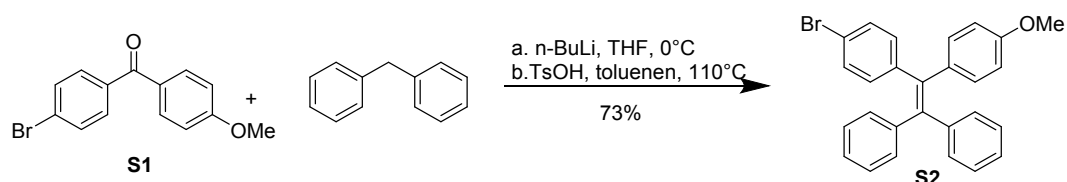
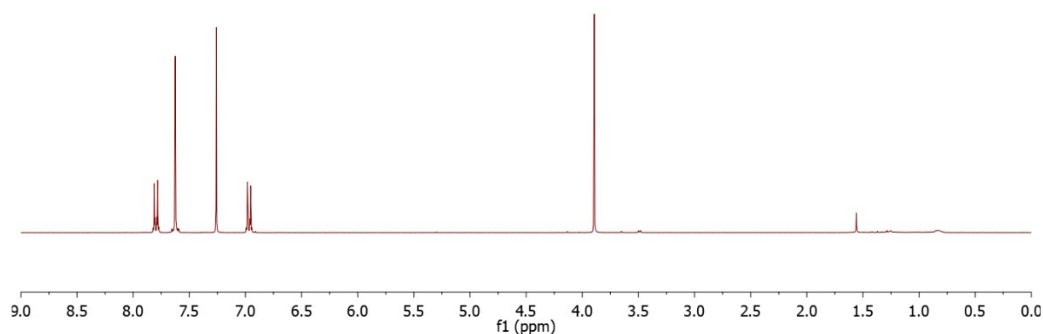
L. Han, S.Q. Zhu, H.W. Ma, P.B. Liu, Y. Li, *et al. Macromolecules*, **2018**, *51*, 6209-6217

4-bromo-4'-methoxybenzophenone (S1):

To a solution of 4-bromobenzoylchloride(2 g, 9.2 mmol, 1 eq.) and aluminum chloride (AlCl₃, 1.82 g, 13.8 mmol, 1.5 eq.) in dry CH₂Cl₂ (14 mL) was added anisole (1.6 g, 13.8 mmol, 1.5 eq., 1.62 mL) at 0°C during 4h. The reaction was quenched by HCl aqueous solution (20 mL, 2M), diluted with CH₂Cl₂ (30 mL) and separated. The aqueous layer was extracted with CH₂Cl₂ (2×20 mL). The combined organic layer was washed dried (MgSO₄), concentrated and purified with silica gel column chromatography (Cyclohexane:CH₂Cl₂ = 1:3) to afford compound **S1** (2.66 g, 99%) as a pure white powder.

R_f = 0.15 (Cyclohexane:CH₂Cl₂ = 1:1)

CDCl₃



B. Liu., J. Liu. PCT Int. Appl. (2018), WO 2018030957 A1 20180215

4-bromo-4'-methoxytetraphenylethene (**S2**):

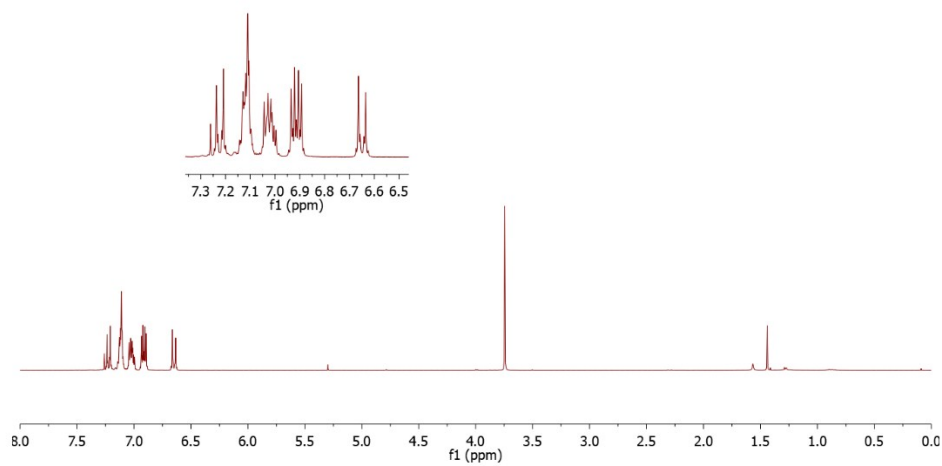
To a solution of diphenylmethane (1.4 g, 8.3 mmol, 1.2 eq.) in dry THF (30 mL) was added *n*-butyllithium (540 mg, 8.3 mmol, 1.2 eq., 3.4 mL, 2.5 M in hexane) dropwise at 0°C and the resulting solution was stirred at 0°C under argon during 45 min. A solution of compound **S1** (2 g, 6.9 mmol, 1 eq.) in dry THF (20 mL) was then added in the reaction. The solution was stirred at RT under argon during 6 h then quenched with saturated NH₄Cl aqueous solution (40 mL). The solvent was evaporated off and the aqueous layer was extracted with CH₂Cl₂ (4×30 mL). The combined organic layers were washed with brine (3×30 mL), dried (MgSO₄) and concentrated. *p*-Toluenesulfonic acid (TsOH, 240 mg, 1.4 mmol, 0.2 eq.) was added to the solution of crude product in toluene (100 mL). The resulting solution was stirred at 110°C during 18 h. The solvent was evaporated off and the residue dissolved in CH₂Cl₂ (70 mL), washed with saturated aqueous NaHCO₃ (2×50 mL), brine (50 mL), dried (MgSO₄), concentrated and purified by silica gel column chromatography (Cyclohexane:CH₂Cl₂ = 8:1) to obtain compound **S2** (2.21 g, 73%) as pale yellow amorphous solid.

R_f = 0.6 (Cyclohexane:CH₂Cl₂ = 3:1)

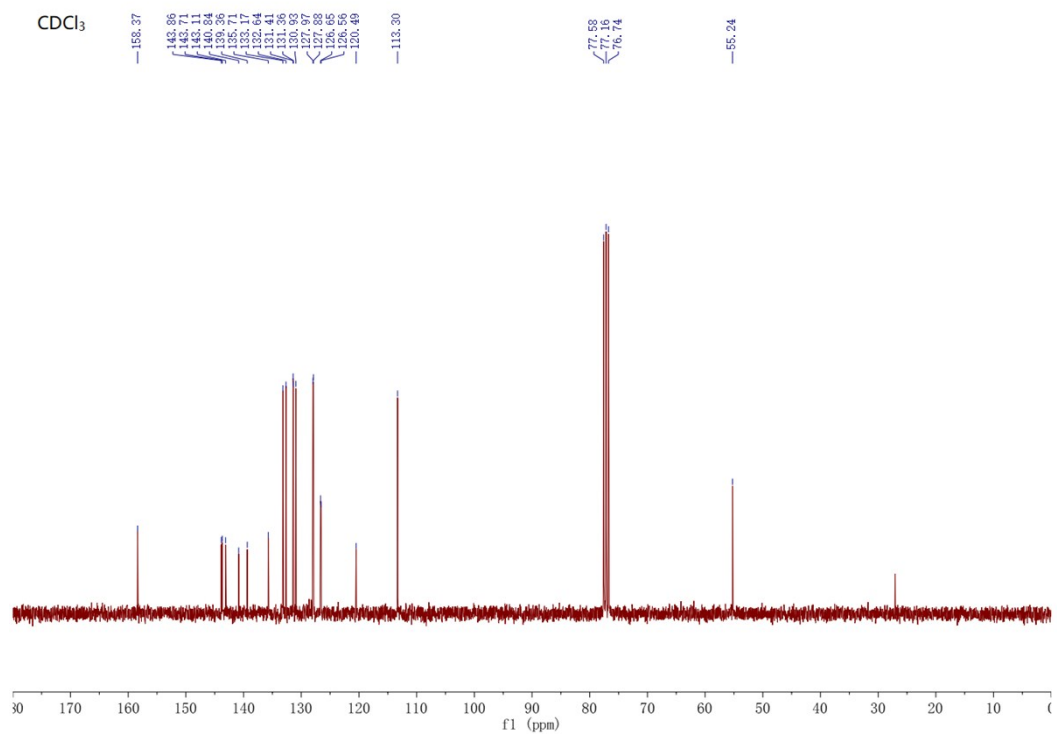
¹H NMR (300 MHz, CDCl₃): δ (ppm) 3.75 (s, 3H, OCH₃), 6.65, (d, 2H, *J* = 8.7 Hz, H-Ar), 6.92 (dd, 4H, *J* = 3.9 Hz, 8.7Hz, H-Ar), 7.01-7.05 (m, 4H, H-Ar), 7.10-7.13 (m, 6H, H-Ar), 7.23 (d, 2H, *J* = 8.7 Hz, H-Ar).

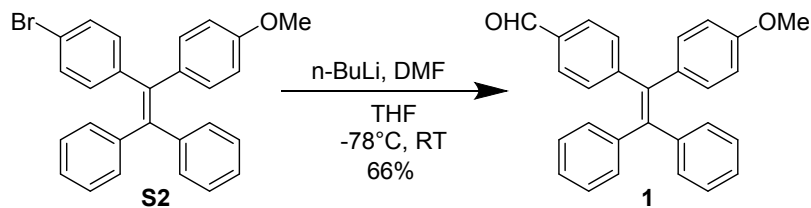
¹³C NMR (75 MHz, CDCl₃): δ (ppm) 55.3 (OCH₃), 113.3 (CH-Ar), 120.5 (C^{Ar}-Br), 126.6 (CH-Ar), 126.7 (CH-Ar), 127.9 (CH-Ar), 128.0 (CH-Ar), 130.9 (CH-Ar), 131.4 (CH-Ar), 131.41 (CH-Ar), 132.6 (CH-Ar), 133.2 (CH-Ar), 135.5 (C^{Ar}-C=C), 139.4 (C^{Ar}-C=C), 140.8 (C^{Ar}-C=C), 143.1 (C^{Ar}-C=C), 143.7 (C=C), 143.9 (C=C), 158.4 (C^{Ar}-OMe).

CDCl₃



CDCl₃





D. Jana, S.Boxi, P. Parui, B. K. Ghorai. *Org. Biomol. Chem.*, **2015**, *13*, 10663-10674

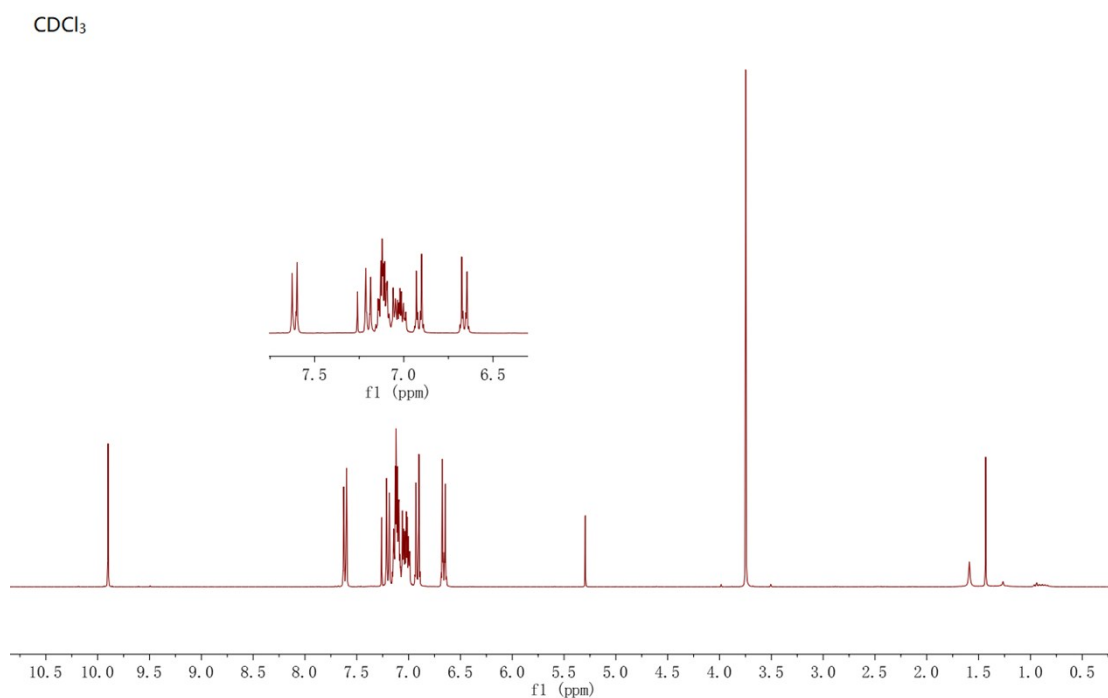
4-methoxy-4'-carbonyltetraphenylethene (1):

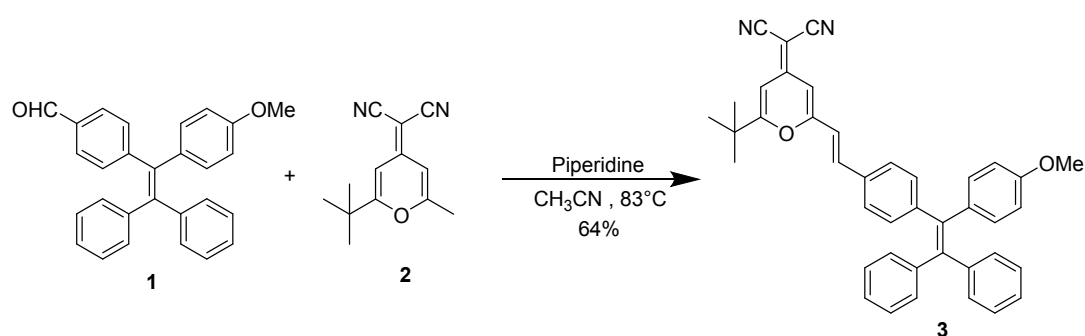
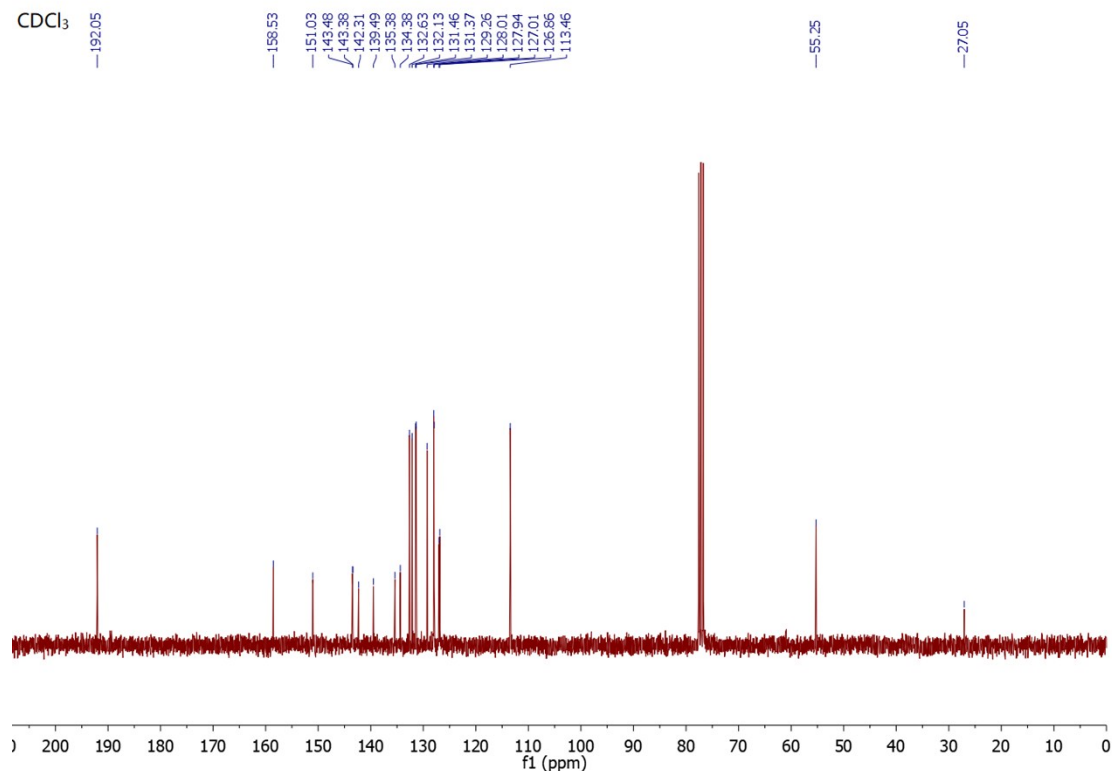
To the solution of compound **S2** (700 mg, 1.6 mmol, 1 eq.) in dry THF (10 mL) was added n-butyllithium (154 mg, 2.4 mmol, 1.5 eq., 1 mL, 2.5M in hexane) at -78°C during 4h. Then 1.2 mL DMF (excessive) was added in the mixture, and stirred at RT during 18h. The reaction was quenched by saturated NH_4Cl aqueous solution (15 mL), and diluted with 100 mL EtOAc. The organic layer was washed with brine (2x50 mL), dried (MgSO_4), concentrated and purified with silica gel column chromatography (Cyclohexane: CH_2Cl_2 = 1:1) to obtain compound **1** (410 mg, 66%) as a yellow amorphous solid.

R_f = 0.21 (Cyclohexane: CH_2Cl_2 = 2:1)

^1H NMR (300 MHz, CDCl_3): δ (ppm) 3.03 (s, 3H, OCH_3), 6.67 (d, 2H, J = 8.7 Hz, H-Ar), 6.92 (d, 2H, J = 9.0 Hz, H-Ar), 6.99-7.06 (m, 4H, H-Ar), 7.0.8-7.26 (m, 6H, H-Ar), 7.62 (d, 2H, J = 8.1 Hz, H-Ar), 9.90 (s, 1H, CHO).

^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 55.3 (OCH_3), 113.5 (CH-Ar), 126.9 (CH-Ar), 127.0 (CH-Ar), 127.94 (CH-Ar), 128.01 (CH-Ar), 129.3 (CH-Ar), 131.4 (CH-Ar), 131.5 (CH-Ar), 132.6 (CH-Ar), 133.2 (CH-Ar), 134.4 ($\text{C}^{\text{Ar-C=C}}$), 135.8 ($\text{C}^{\text{Ar-C=C}}$), 139.5 ($\text{C}^{\text{Ar-C=C}}$), 142.3 ($\text{C}^{\text{Ar-C=C}}$), 143.38 (C=C), 143.43 (C=C), 151.03 ($\text{C}^{\text{Ar-CHO}}$), 158.4 ($\text{C}^{\text{Ar-OMe}}$), 192.1 (CHO).





(E)-2-{2-[4-[2,2-diphenyl-1-(4-methoxyphenyl)-1-vinyl]styryl]-6-(tert-butyl)-4H-pyran-4-ylidene}-propanedinitrile (3):

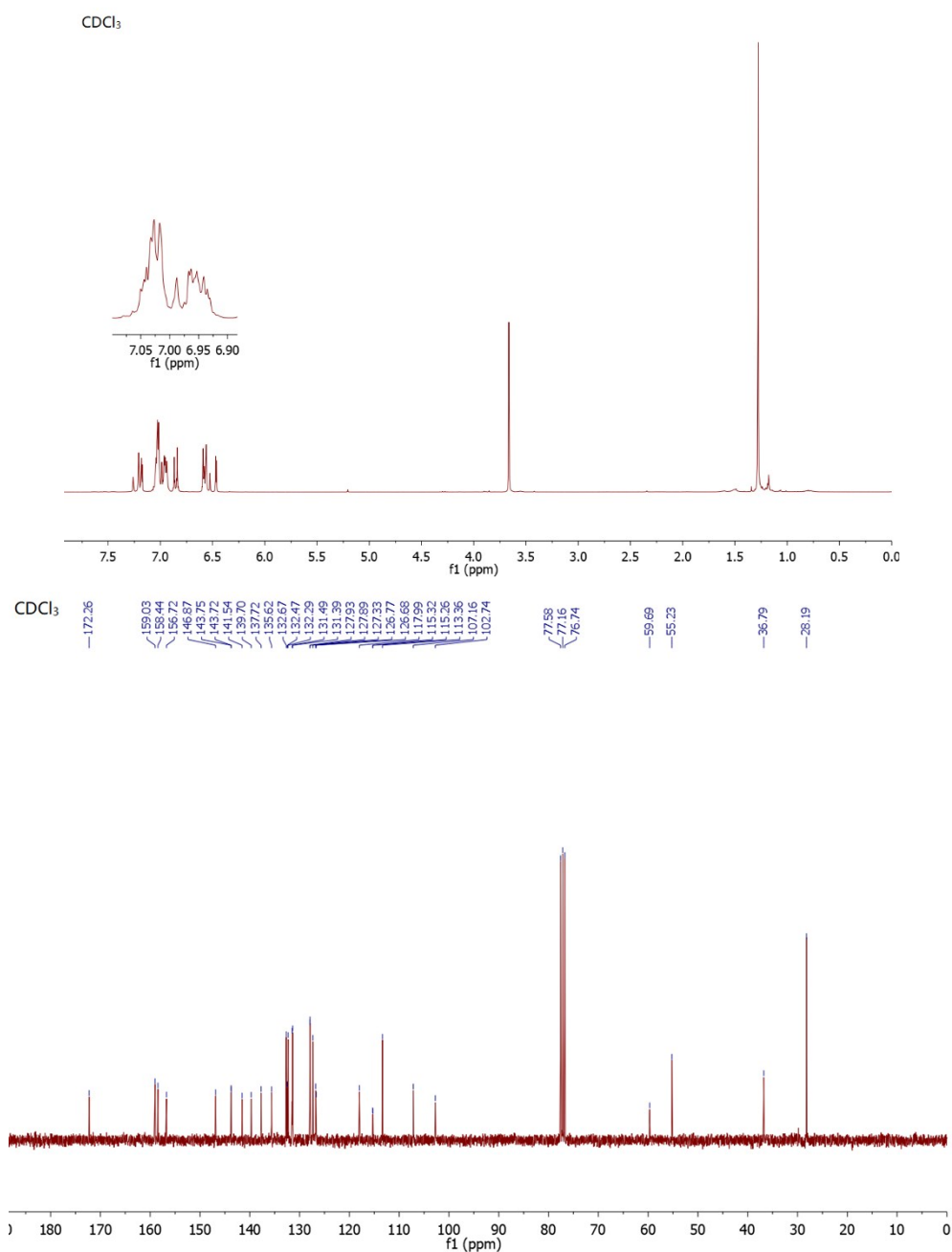
To the solution of compound **1** (400 mg, 1.03 mmol, 1 eq.) and compound **2**^[1] (241 mg, 1.13 mmol, 1.1eq.) in CH₃CN (12 mL) was added piperidine (175 mg, 2.06 mmol, 2 eq., 0.21 mL). The resulting solution was stirred at 83°C during 2 days. The mixture was evaporated and diluted with EtOAc (50 mL), wash with brine (2x50 mL). The organic layer was dried (MgSO₄), concentrated and purified with silica gel column chromatography (Cyclohexane:EtOAc = 3.5:1) to obtain compound **3** (410 mg, 64%) as a red amorphous solid.

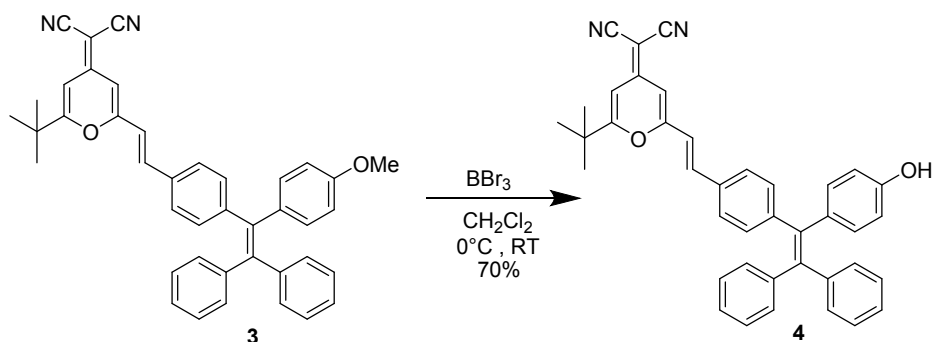
R_f = 0.17 (Cyclohexane:CH₂Cl₂ = 1:4)

¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.37 (s, 9H, C(CH₃)₃), 3.75 (s, 3H, OCH₃), 6.57 (d, 1H, J = 2.1 Hz, H-3pyran), 6.60-6.67 (d, 1H, H-3pyran), 6.61-6.68 (m, 4H, H-5pyran, 2xH-Ar, HC=CH-Ph), 6.94 (d, 2H, J = 8.7 Hz, H-Ar), 7.02-7.08 (m, 5H, H-Ar), 7.09-7.14 (m, 7H, H-Ar), 7.27-7.35 (m, 3H, 2xH-Ar, HC=CH-Ph).

^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 28.2 ($\text{C}(\text{CH}_3)_3$), 36.8 ($\text{C}(\text{CH}_3)_3$), 55.2 (OCH_3), 59.7 ($\text{C}(\text{CN})_2$), 102.7 (C-3pyran), 107.2 (C-5pyran), 113.4 (CH-Ar), 115.3 (2xCN), 118.0 ($\text{HC}=\text{CH}-\text{Ph}$), 126.7 (CH-Ar), 126.8 (CH-Ar), 127.3 (CH-Ar), 127.9 (CH-Ar), 127.93 (CH-Ar), 131.4 (CH-Ar), 131.5 (CH-Ar), 132.3 (CH-Ar), 132.5 ($\text{C}^{\text{Ar}}-\text{CH}=\text{CH}-\text{Pyran}$), 132.7 (CH-Ar), 135.6 ($\text{C}^{\text{Ar}}-\text{C}=\text{C}$), 137.7 ($\text{HC}=\text{CH}-\text{Ph}$), 137.7 ($\text{C}^{\text{Ar}}-\text{C}=\text{C}$), 141.5 ($\text{C}^{\text{Ar}}-\text{C}=\text{C}$), 143.72 (C=C), 143.75 (C=C), 146.9 ($\text{C}^{\text{Ar}}-\text{C}=\text{C}$), 156.7 (C-6pyran), 158.4 ($\text{C}^{\text{Ar}}-\text{OME}$), 159.0 (C-2pyran), 172.3 (C-4pyran).

HR-ESI-MS m/z : calcd. for $\text{C}_{41}\text{H}_{35}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$ 587.2699, found 587.2693.





(E)-2-(2-(4-[2,2-diphenyl-1-(4-hydroxyphenyl)-1-vinyl]styryl)-6-(tert-butyl)-4H-pyran-4-ylidene)propanedinitrile (4):

To a solution of compound **3** (280 mg, 0.48 mmol, 1 eq.) in dry CH₂Cl₂ (10 mL) was added in the solution of BBr₃ (154 mg, 0.62 mmol, 1.3 eq., 0.62 mL, 1 M in CH₂Cl₂) at 0°C. The resulting solution was stirred at 0°C firstly, and then stirred at RT during 18h. The solution was poured into ice water (50 mL), and solid compound was dissolved with EtOAc (100-150 mL). The organic layer after extracting aqueous solution with EtOAc (2×40 mL), was combined, washed with brine (50 mL x 3), dried (MgSO₄), concentrated, and purified with silica gel column chromatograph (CH₂Cl₂) to obtain compound **4** (204 mg, 50%) as a red amorphous solid.

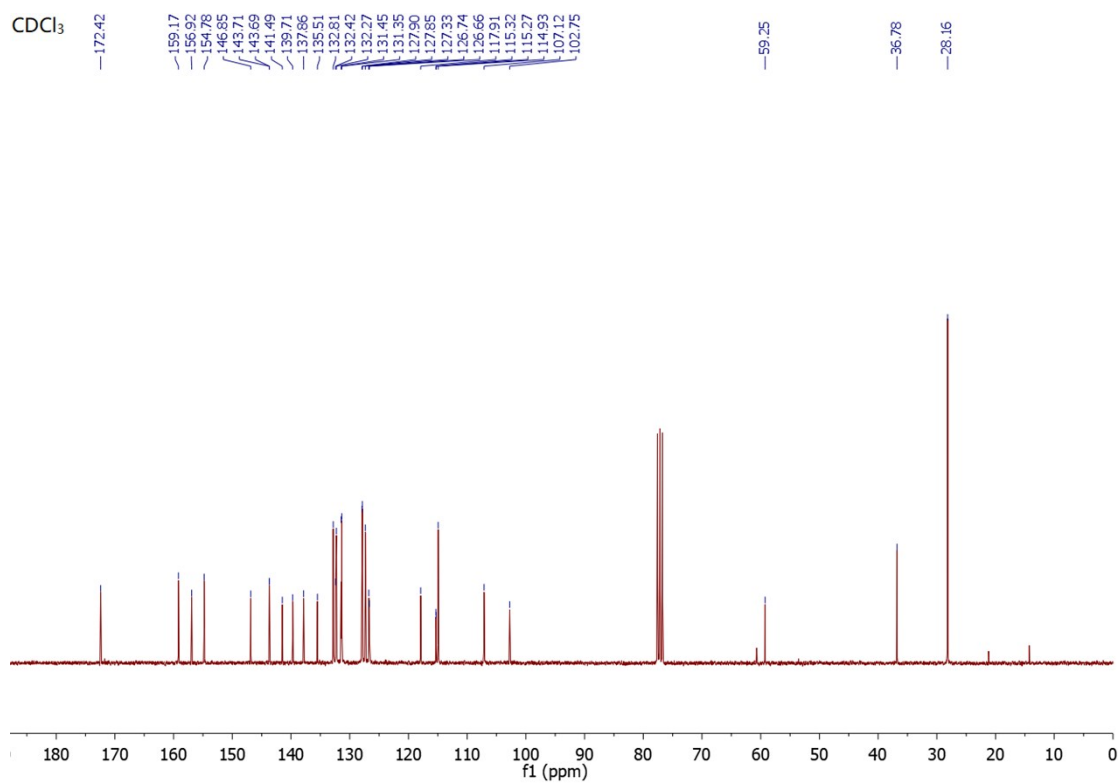
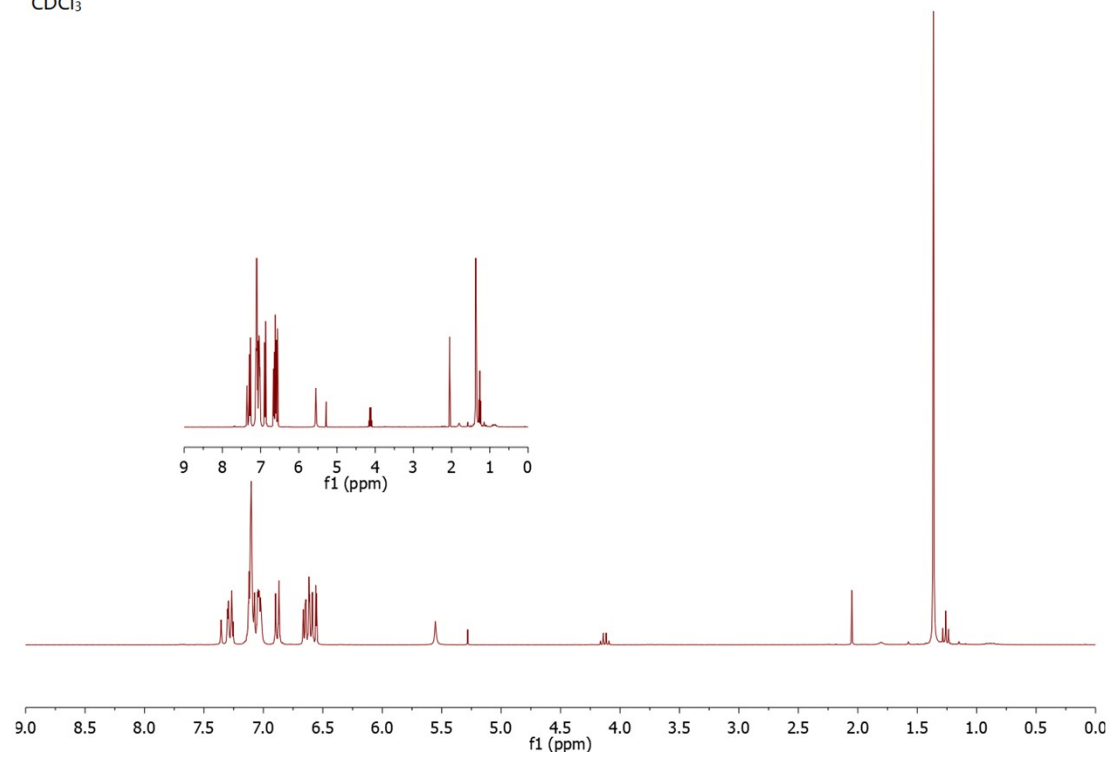
R_f = 0.26 (CH₂Cl₂:MeOH = 70:1)

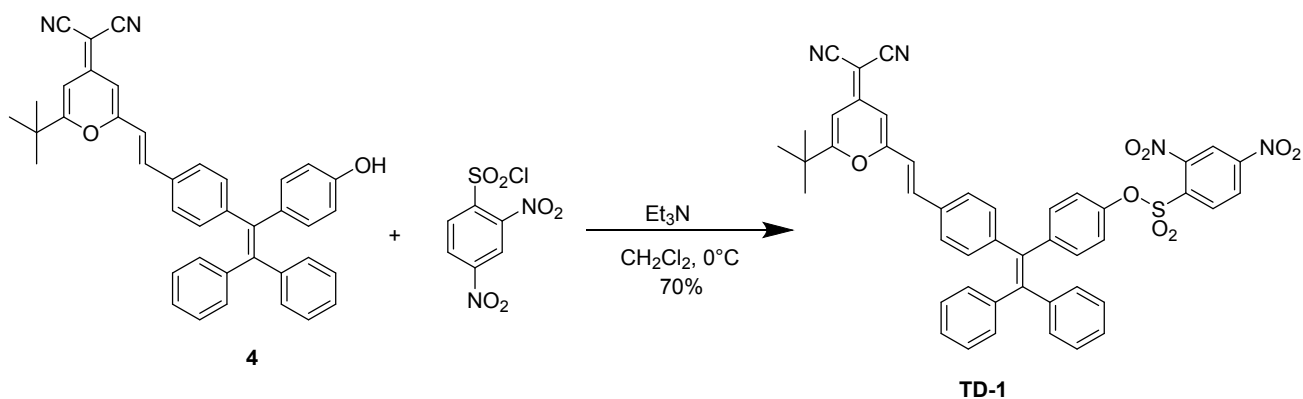
¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.37 (s, 9H, C(CH₃)₃), 6.57 (d, 1H, J = 2.1 Hz, H-3pyran), 6.60-6.67 (m, 4H, H-5pyran, 2xH-Ar, HC=CH-Ph), 6.89 (d, 2H, J = 8.4 Hz, H-Ar), 7.02-7.13 (m, 12H, H-Ar), 7.27-7.36 (m, 3H, 2xH-Ar, HC=CH-Ph).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 28.2 (C(CH₃)₃), 36.8 (C(CH₃)₃), 59.3 (C(CN)₂), 102.8 (C-3pyran), 107.1 (C-5pyran), 114.9 (CH-Ar), 115.3 (2xCN), 118.0 (HC=CH-Ph), 126.66 (CH-Ar), 126.7 (CH-Ar), 127.3 (CH-Ar), 127.85 (CH-Ar), 127.9 (CH-Ar), 131.4 (CH-Ar), 131.5 (CH-Ar), 132.3 (CH-Ar), 132.4 (C^{Ar}-CH=CH-Pyran), 132.8 (CH-Ar), 135.5 (C^{Ar}-C=C), 137.9 (HC=CH-Ph), 139.7 (C^{Ar}-C=C), 141.5 (C^{Ar}-C=C), 143.69 (C=C), 143.71 (C=C), 146.9 (C^{Ar}-C=C), 154.8 (C-6pyran), 156.9 (C^{Ar}-OH), 159.2 (C-2pyran), 172.4 (C-4pyran).

HR-ESI-MS *m/z*: calcd. for C₄₀H₃₃N₂O₂ [M+H]⁺ 573.2542, found 573.2552.

CDCl₃





(E)-2-{2-[4-[2,2-diphenyl-1-(4-[2,4-dinitrophenylsulfonyl]phenyl)-1-vinyl]styryl]-6-(tert-butyl)-4H-pyran-4-ylidene}-propanedinitrile (TD-1):

To a solution of 2,4-dinitrobenzenesulfonyl chloride (compound **5**, 298 mg, 1.12 mmol, 16 eq.) and Et₃N (128 mg, 1.26 mmol, 18 eq., 0.16 mL) in CH₂Cl₂ (7 mL) was added the solution of compound **4** (40 mg, 0.07 mmol, 1eq.) in CH₂Cl₂ (3 mL) at 0°C. The resulting solution was stirred at 0°C under argon during 3h. When compound **4** disappeared on TLC board, the mixture was evaporated and purified with silica gel column chromatography (Cyclohexane:CH₂Cl₂ = 1:4) to obtain compound **TD-1** (39 mg, 70%) as a red amorphous solid.

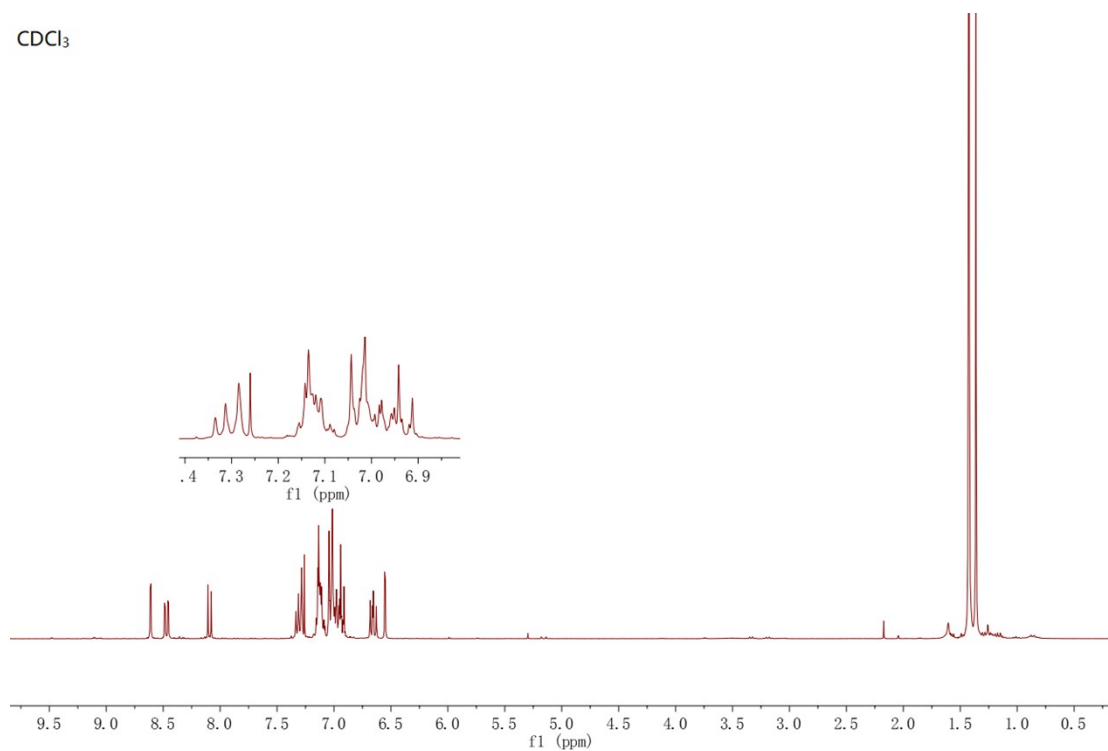
R_f = 0.4 (CH₂Cl₂)

¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.36 (s, 9H, C(CH₃)₃), 6.56 (d, 1H, *J* = 2.1 Hz, H-3pyran), 6.65 (d, 1H, *J* = 2.1 Hz, H-5pyran), 6.66 (d, 1H, *J* = 16.2 Hz, HC=CH-Ph), 6.91-7.04 (m, 10H, H-Ar), 7.11-7.16 (m, 6H, H-Ar), 7.28-7.34 (m, 3H, 2xH-Ar, HC=CH-Ph), 8.10 (d, 1H, *J* = 8.7 Hz, H-Ar2), 8.47 (dd, 1H, *J* = 2.1 Hz, 8.7 Hz, H-Ar2), 8.61 (d, 1H, *J* = 2.4 Hz, H-Ar2).

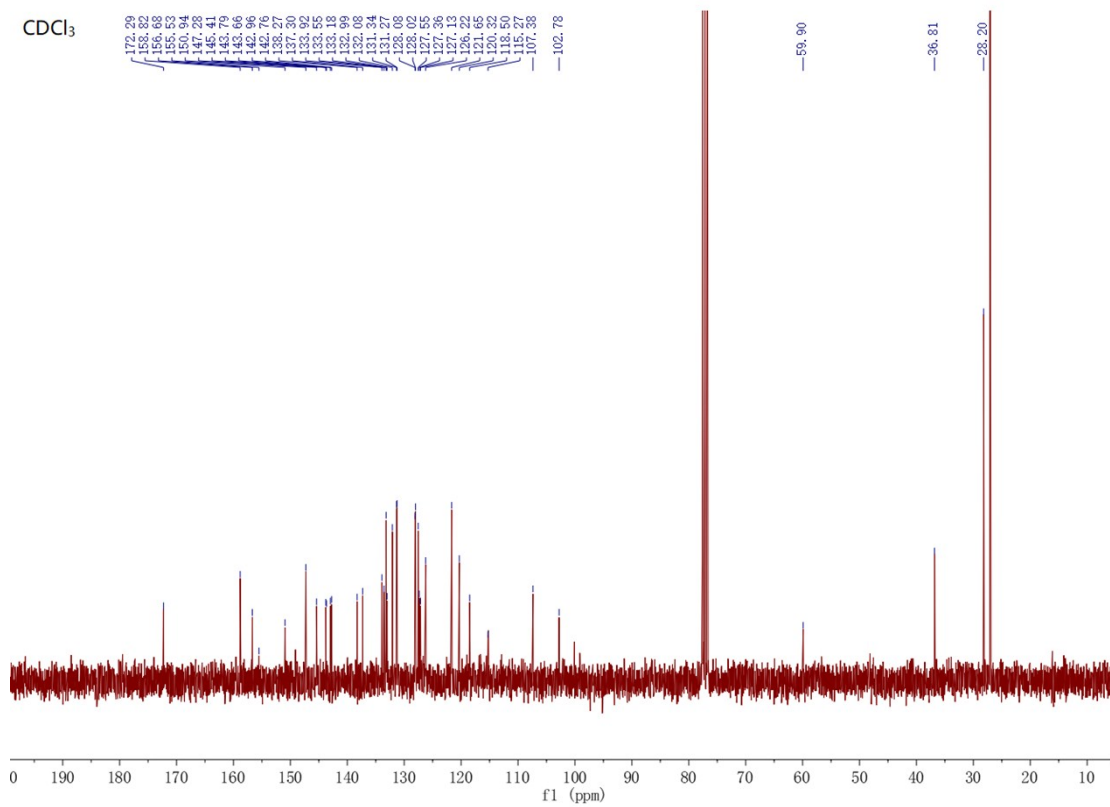
¹³C NMR (75 MHz, CDCl₃): δ (ppm) 28.2 (C(CH₃)₃), 36.8 (C(CH₃)₃), 59.9 (C(CN)₂), 102.8 (C-3pyran), 107.4 (C-5pyran), 115.3 (CH-Ar), 115.3 (2xCN), 118.5 (HC=CH-Ph), 120.3 (CH-Ar2), 121.7 (CH-Ar), 126.2 (CH-Ar2), 127.1 (CH-Ar), 127.4 (CH-Ar), 127.08 (CH-Ar), 128.02 (CH-Ar), 131.27 (CH-Ar), 131.34 (CH-Ar), 132.1 (CH-Ar), 133.0 (C^{Ar}-CH=CH-Pyran), 133.2 (CH-Ar), 133.6 (C^{Ar}-C=C), 133.9 (CH-Ar2), 137.3 (HC=CH-Ph), 138.3 (C^{Ar}-C=C), 142.8 (C^{Ar2}-NO₂), 142.9 (C^{Ar2}-NO₂), 143.7 (C=C), 143.8 (C=C), 145.4 (C^{Ar}-C=C), 147.3 (C^{Ar}-C=C), 150.1 (C-6pyran), 155.5 (C^{Ar2}-SO₂), 156.9 (C^{Ar}-OSO₂), 158.9 (C-2pyran), 172.3 (C-4pyran).

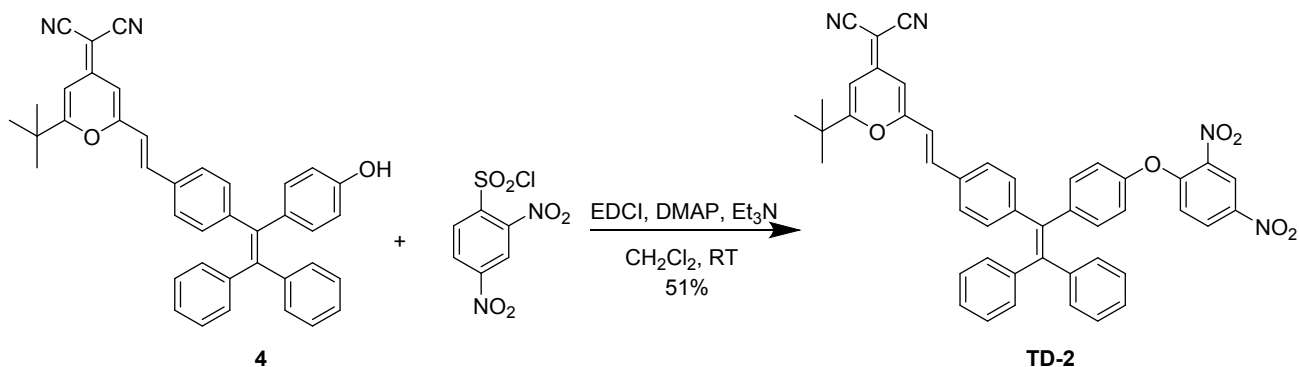
HR-ESI-MS *m/z*: calcd. for C₄₆H₃₅N₄O₈S [M+H]⁺ 803.2176, found 803.2170.

CDCl₃



CDCl₃





(E)-2-{2-[4-[2,2-diphenyl-1-(4-[2,4-dinitrophenoxy]phenyl)-1-vinyl]styryl]-6-(tert-butyl)-4H-pyran-4-ylidene}-propanedinitrile (TD-2):

To a solution of compound **4** (50 mg, 0.087 mmol, 1 eq.), 2,4-dinitrobenzenesulfonyl chloride (compound **5**, 298 mg, 1.12 mmol, 16 eq.), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDCI, 84 mg, 0.44 mmol, 5 eq.) and 4-dimethylaminopyridine (DMAP, 11 mg, 0.087 mmol, 1 eq.) in CH₂Cl₂ (10 mL) was added Et₃N (151 mg, 1.49 mmol, 17 eq., 0.2 mL). The resulting solution was stirred at RT under argon during 20h. The mixture was diluted with CH₂Cl₂ (50 mL), washed with HCl aqueous solution (30 mL, 2M) and brine (2×50 mL). The organic layer was dried (MgSO₄), concentrated and purified with silica gel column chromatography (Cyclohexane:CH₂Cl₂ = 1:3) to obtain compound **TD-2** (33 mg, 51%) as a red amorphous solid.

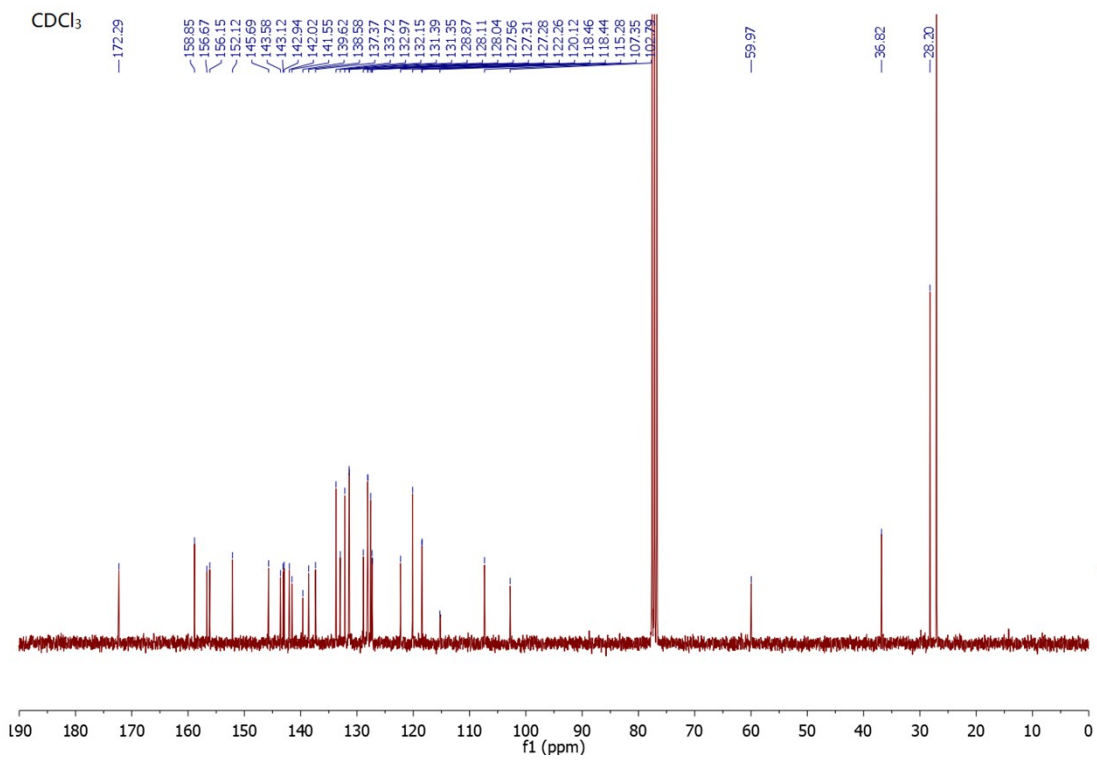
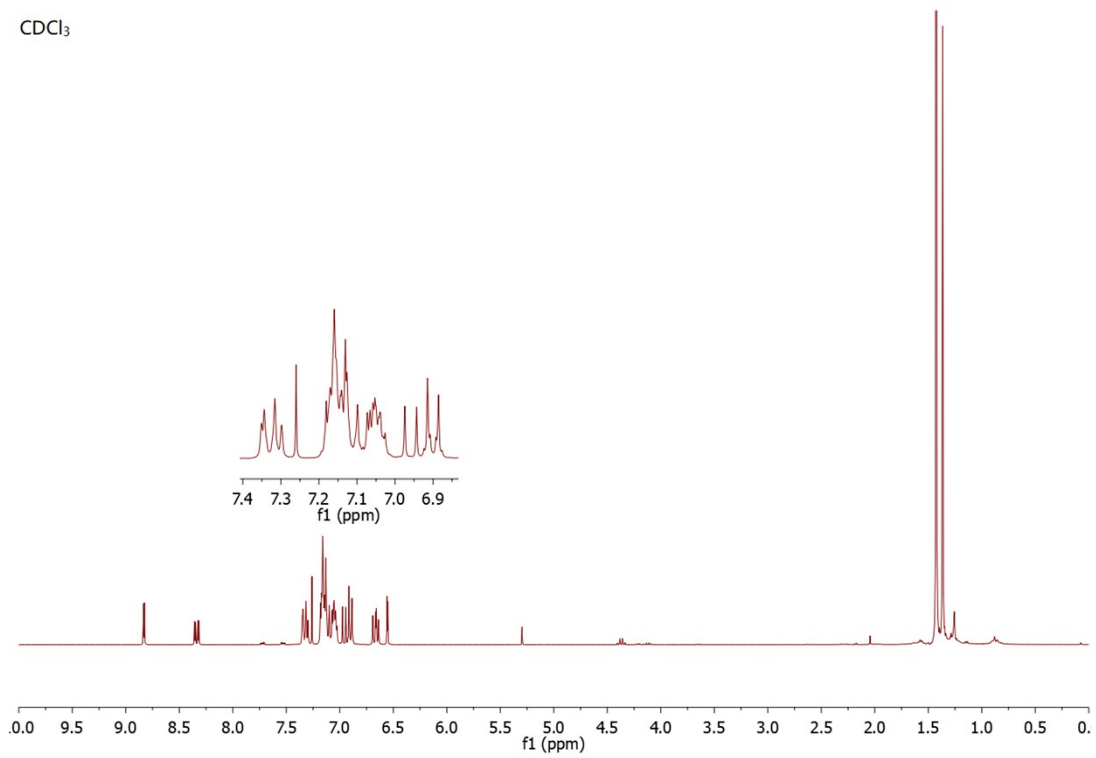
R_f = 0.7 (CH₂Cl₂)

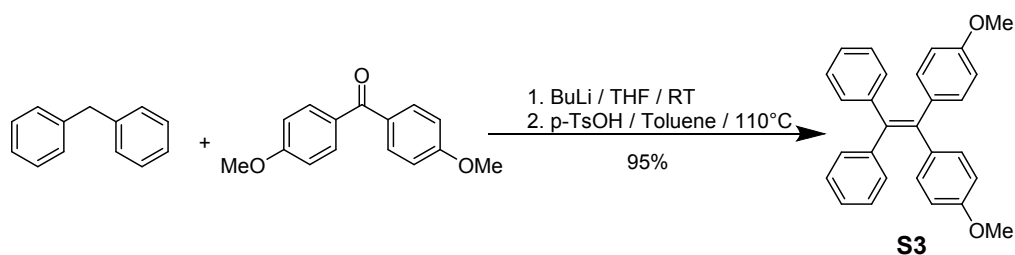
¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.37 (s, 9H, C(CH₃)₃), 6.56 (d, 1H, J = 2.1 Hz, H-3pyran), 6.66 (d, 1H, J = 2.1 Hz, H-5pyran), 6.67 (d, 1H, J = 15.9 Hz, HC=CH-Ph), 6.91 (d, 1H, J = 8.7 Hz, H-Ar), 6.95 (d, 1H, J = 9.0 Hz, H-Ar2) 7.03-7.10 (m, 5H, H-Ar), 7.12-7.19 (m, 9H, H-Ar), 7.30-7.35 (m, 3H, 2xH-Ar, HC=CH-Ph), 8.34 (dd, 1H, J = 3.0 Hz, 9.3 Hz, H-Ar2), 8.61 (d, 1H, J = 2.7 Hz, H-Ar2).

¹³C NMR (75 MHz, CDCl₃): δ (ppm) 28.2 (C(CH₃)₃), 36.8 (C(CH₃)₃), 60.0 (C(CN)₂), 102.8 (C-3pyran), 107.4 (C-5pyran), 115.3 (2xCN), 118.44 (CH-Ar2), 118.46 (HC=CH-Ph), 120.1 (CH-Ar), 122.3 (CH-Ar2), 127.28 (CH-Ar), 127.31 (CH-Ar), 127.6 (CH-Ar), 128.04 (CH-Ar), 128.11 (CH-Ar), 128.9 (CH-Ar2), 131.35 (CH-Ar), 131.39 (CH-Ar), 132.2 (CH-Ar), 133.0 (C^{Ar}-CH=CH-Pyran), 133.7 (CH-Ar), 137.4 (HC=CH-Ph), 138.6 (C^{Ar}-C=C), 139.6 (C^{Ar}-C=C), 141.6 (C^{Ar2}-NO₂), 142.0 (C^{Ar2}-NO₂), 142.94 (C=C), 143.12 (C=C), 143.6 (C^{Ar}-C=C), 145.7 (C^{Ar}-C=C), 152.1 (C-6pyran), 155.5 (C^{Ar2}-O), 156.7 (C^{Ar}-O), 158.9 (C-2pyran), 172.3 (C-4pyran).

HR-ESI-MS *m/z*: calcd. for C₄₆H₃₅N₄O₆ [M+2Na]²⁺ 739.2557, found 739.2551.

CDCl₃





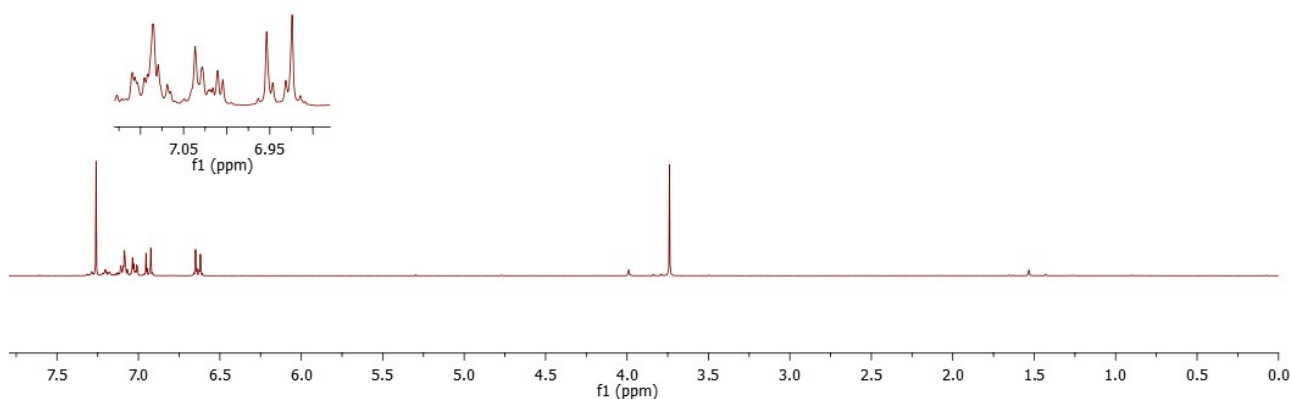
HT Feng, JB Xiong, YS Zheng, B Pan, CH Zhang, L Wang, YS Xie *Chem. Mater.* **2015**, *27*, 7812-7819.

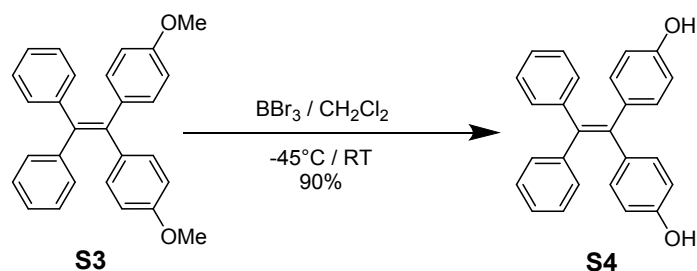
1,1-Di-(4-methoxyphenyl)-2,2-di-phenyl-ethylene (S3):

To a solution of diphenylmethane (3 g, 17.9 mmol, 1.3 eq.) in dry THF (30 mL) was added *n*-butyllithium (1.14 g, 17.9 mmol, 1.3 eq., 2.5 M in hexane) dropwise at 0°C and the resulting solution was stirred at 0°C under argon during 45 min. A solution of 4,4'-dimethoxybenzophenone (2.6 g, 13.8 mmol, 1 eq.) in dry THF (20 mL) was then added in the reaction. The solution was stirred at RT under argon during 3.5 h then quenched with aqueous NH₄Cl saturated (40 mL). The solvent was evaporated off and the aqueous layer was extracted with CH₂Cl₂ (4×30 mL). The combined organic layers were washed with brine (3×30 mL), dried (MgSO₄) and concentrated. *p*-Toluenesulfonic acid (480 mg, 2.76 mmol, 0.2 eq.) was added to the solution of crude product in toluene (70 mL). The resulting solution was stirred at 110°C during 18 h. The solvent was evaporated off and the residue dissolved in CH₂Cl₂ (70 mL), washed with saturated aqueous NaHCO₃ (2×50 mL), brine (50 mL), dried (MgSO₄), concentrated and purified by silica gel column chromatography (Cyclohexane:EtOAc = 10:1) to obtain compound **S3** (4.43 g, 95%) as white amorphous solid.

R_f = 0.26 (Cyclohexane:EtOAc, 10:1)

CDCl₃





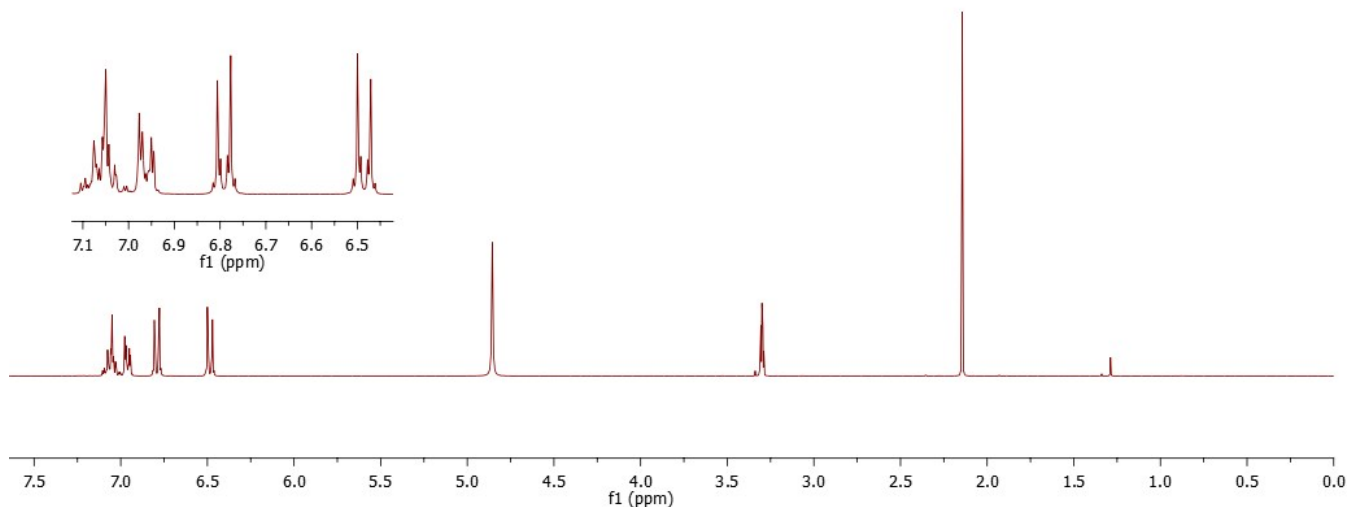
Mandapati V. Ramakrishnam raju and H.CH. Lin *Org. Lett.* **2014**, *16*, 5564-5567.

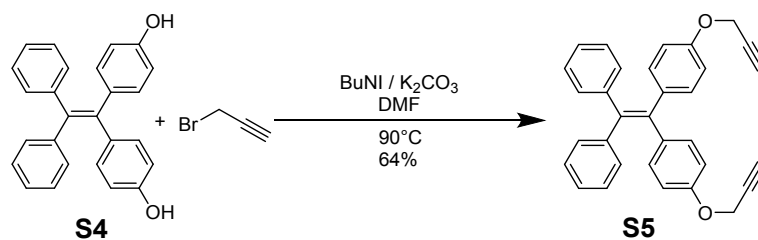
1,1-Di-(4-hydroxyphenyl)-2,2-di-phenyl-ethylene (S4):

To a solution of compound **S3** (2 g, 5.1 mmol, 1 eq.) in dry CH_2Cl_2 (100 mL) was added BBr_3 (7.5 g, 30.6 mmol, 6 eq., 1 M in CH_2Cl_2) at -45°C . The resulting solution was stirred at -45°C under argon during 1 h then at RT during 6 h. The reaction was poured into 2 M HCl (40 mL), and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2×30 mL). The organic layers were combined then washed with brine (50 mL), dried (MgSO_4), concentrated and purified by silica gel column chromatography (CH_2Cl_2 :MeOH = 100:1) to obtain compound **S4** (1.75 g, 90%) as pale yellow amorphous solid.

$R_f = 0.12$ (CH_2Cl_2)

MeOD- d_4





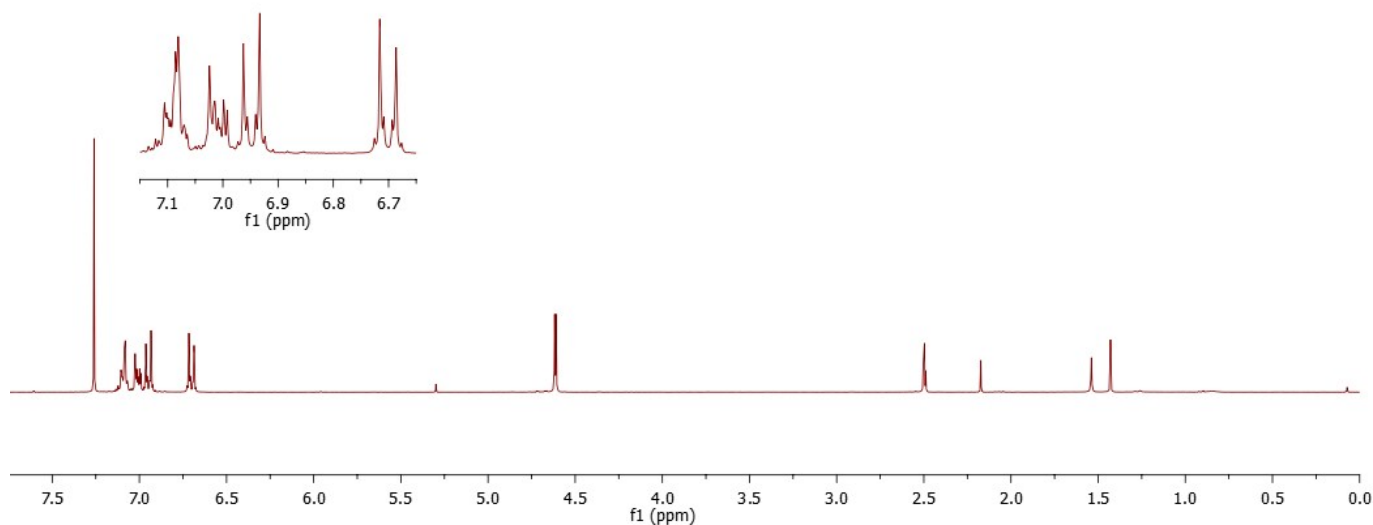
AX Ding, Q Tang, YG Gao, YD Shi, A Uzair, ZL Lu. *ACS Appl. Mater. Interfaces*, **2016**, *8*, 14367-14378.

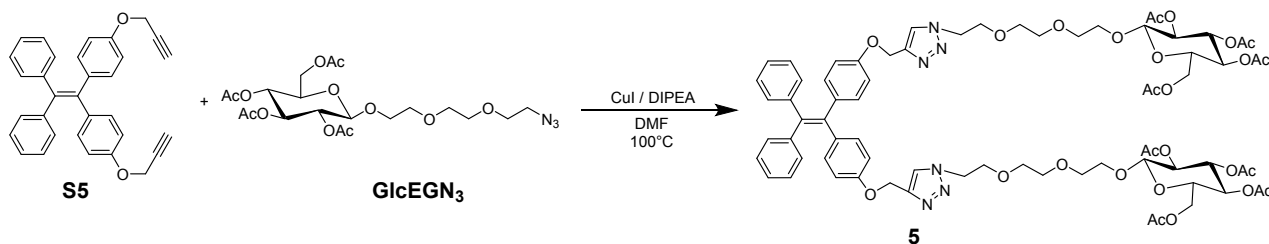
1,1-Di-[4-(2-propyn-1-yloxy)phenyl]-2,2-di-phenyl-ethylene (S5):

To a solution of compound **S4** (1.75 g, 4.6 mmol, 1 eq.), K₂CO₃ (3.8 g, 27.6 mmol, 6 eq.), tetrabutylammonium iodide (6.8 g, 18.5 mmol, 4 eq.) in DMF (50 mL) was added propargyl bromide (2.7 g, 18.5 mmol, 4 eq., 2.5 mL, 80 w% in toluene). The resulting mixture was stirred at 90°C under argon during 18 h. The solvent was evaporated off and the residue diluted with EtOAc (50 mL) and filtered. The filtrate was washed with brine (3×40 mL), dried (MgSO₄), concentrated, and purified by silica gel column chromatography (Cyclohexane:EtOAc = 8:1) to obtain compound **S5** (1.43 g, 64%) as white amorphous solid.

R_f = 0.67 (CH₂Cl₂)

CDCl₃





1,1-Di-(4-{1-[1-(2,3,4,6-tetra-*O*-acetyl- β -D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-yl-methoxy}phenyl)-2,2-di-phenyl-ethylene (5):

To a solution of compound **S5** (385 mg, 0.88 mmol, 1 eq.), compound **GlcEGN₃** (1.3 g, 2.63 mmol, 3 eq.), copper(I) iodide (165 mg, 0.88 mmol, 1 eq.) in DMF (12 mL) was added *N,N*-diisopropylethylamine (340 mg, 2.63 mmol, 3 eq., 0.45 mL). The resulting mixture was stirred under microwave activation at 100°C during 30 min. The mixture was diluted with EtOAc (50 mL), washed with saturated aqueous EDTA (2×40 mL) and brine (40 mL), dried (MgSO₄), concentrated, and purified by silica gel column chromatography (CH₂Cl₂:MeOH = 30:1) to obtain compound **5**, (1.11 g, 87%) as pale yellow amorphous solid.

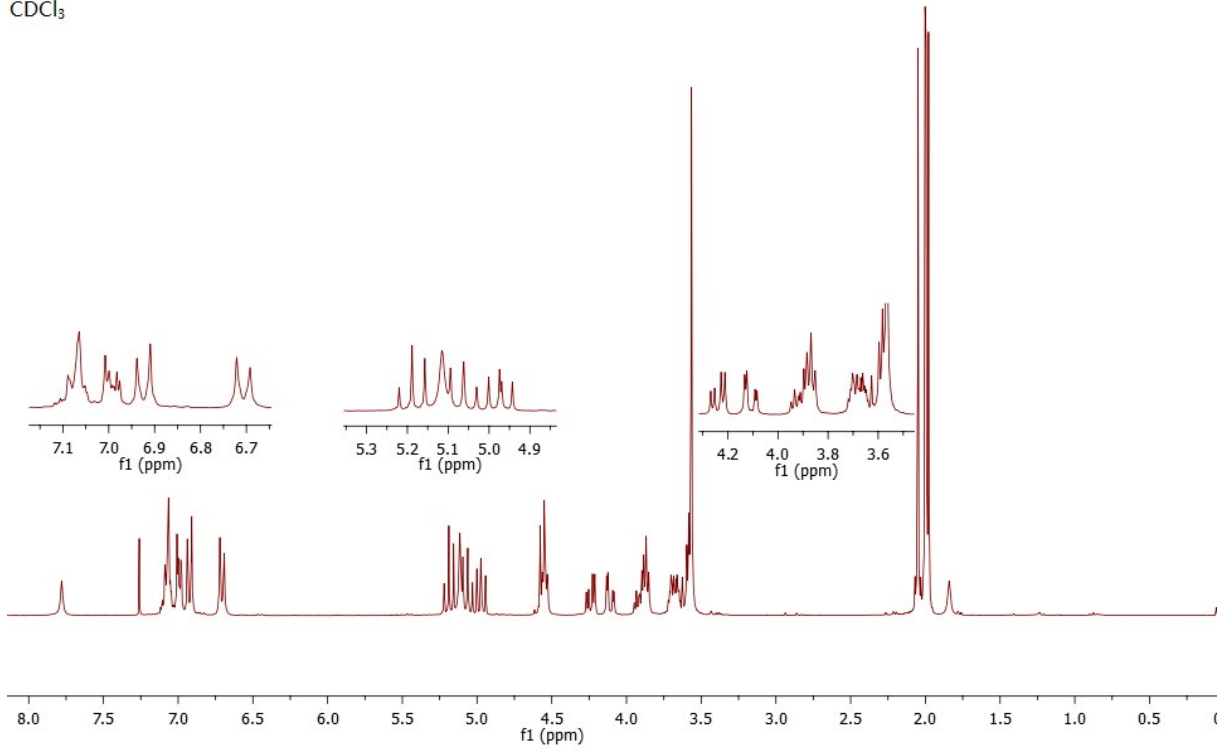
R_f = 0.30 (CH₂Cl₂:MeOH, 40:1)

¹H NMR (300 MHz, CDCl₃): δ (ppm) 1.98, 2.00, 2.01, 2.05 (4s, 4×6H, CH₃CO), 3.57-3.60 (m, 12H, OCH₂CH₂O), 3.63-3.71 (m, 4H, H-5, Glc-OCH₂), 3.85-3.93 (m, 6H, OCH₂CH₂N, Glc-OCH₂), 4.11, (dd, *J* = 2.4 Hz, 12.3 Hz, 2H, H-6'), 4.24 (dd, *J* = 4.5 Hz, 12.3 Hz, 2H, H-6), 4.53-4.58 (m, 6H, H-1, OCH₂CH₂N), 4.97 (dd, *J* = 7.8 Hz, 9.6 Hz, H-2), 5.06 (t, *J* = 9.6 Hz, 2H, H-4), 5.11 (s, 4H, OCH₂-triaz), 5.19 (t, *J* = 9.6 Hz, 2H, H-3), 6.71 (d, *J* = 8.7 Hz, 4H, H-Ar), 6.93 (d, *J* = 8.7 Hz, 4H, H-Ar), 6.98-7.01 (m, 4H, Ph), 7.05-7.09 (m, 6H, Ph), 7.78 (s, 2H, H-triaz).

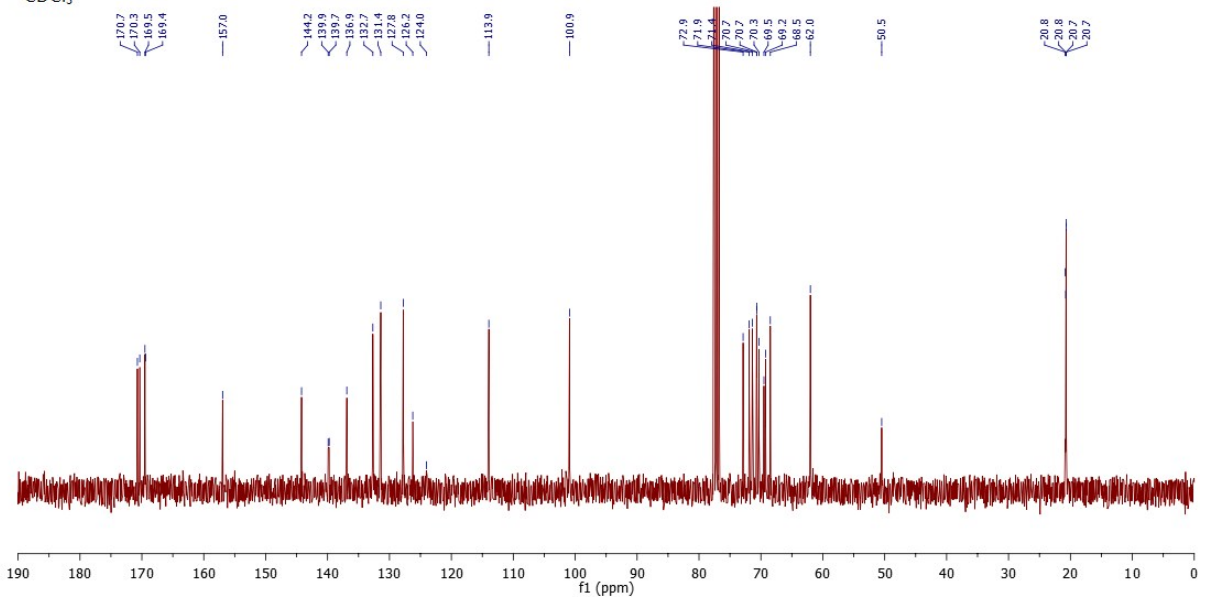
¹³C NMR (75 MHz, CDCl₃): δ (ppm) 20.68, 20.69, 20.76, 20.83 (4×COCH₃), 50.5 (OCH₂CH₂N), 60.2 (C-6), 60.2 (OCH₂-triaz), 68.5 (C-4), 69.2 (Glc-OCH₂), 69.5 (OCH₂CH₂N), 70.3 (OCH₂), 70.66 (OCH₂), 70.68 (OCH₂), 71.4 (C-2), 71.9 (C-5), 72.9 (C-3), 100.9 (C-1), 113.9 (CH-Ar), 124.0 (CH^{triaz}), 126.2 (Ph), 127.8 (Ph), 131.4 (Ph), 132.7 (CH-Ar), 136.9 (C^{Ph}-C=C), 139.7 (C^{Ar}-C=C), 139.9 (C=C), 144.2 (C^{triaz}), 157.0 (C^{Ar}-O), 169.4, 169.5, 170.3, 170.7 (4×COCH₃).

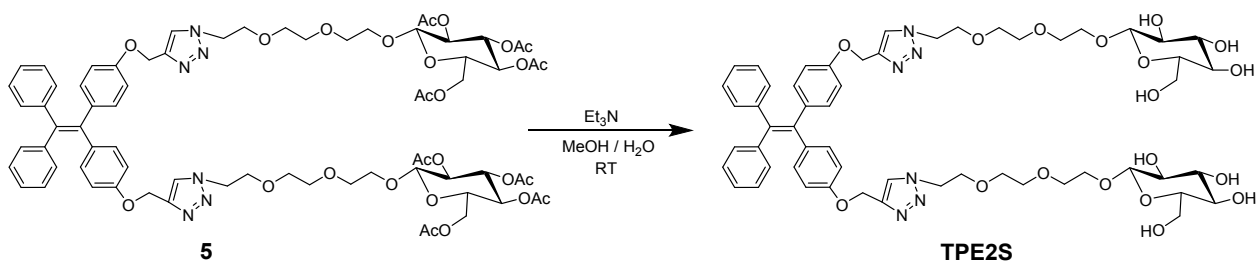
HR-ESI-MS *m/z*: calcd. for C₇₂H₈₈N₆O₂₆ [M+2H]²⁺ 726.2842, found 726.2869.

CDCl₃



CDCl₃





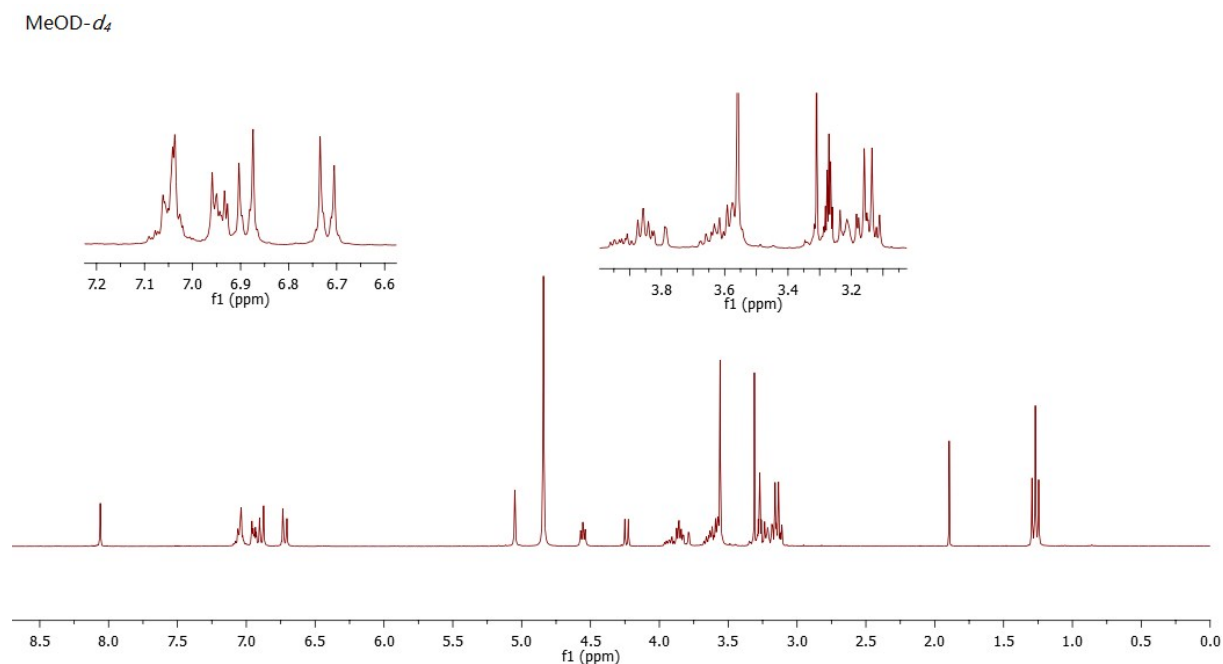
1,1-Di-(4-{1-[1-(β -D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-yl-methoxy}phenyl)-2,2-di-phenyl-ethylene (TPE2S):

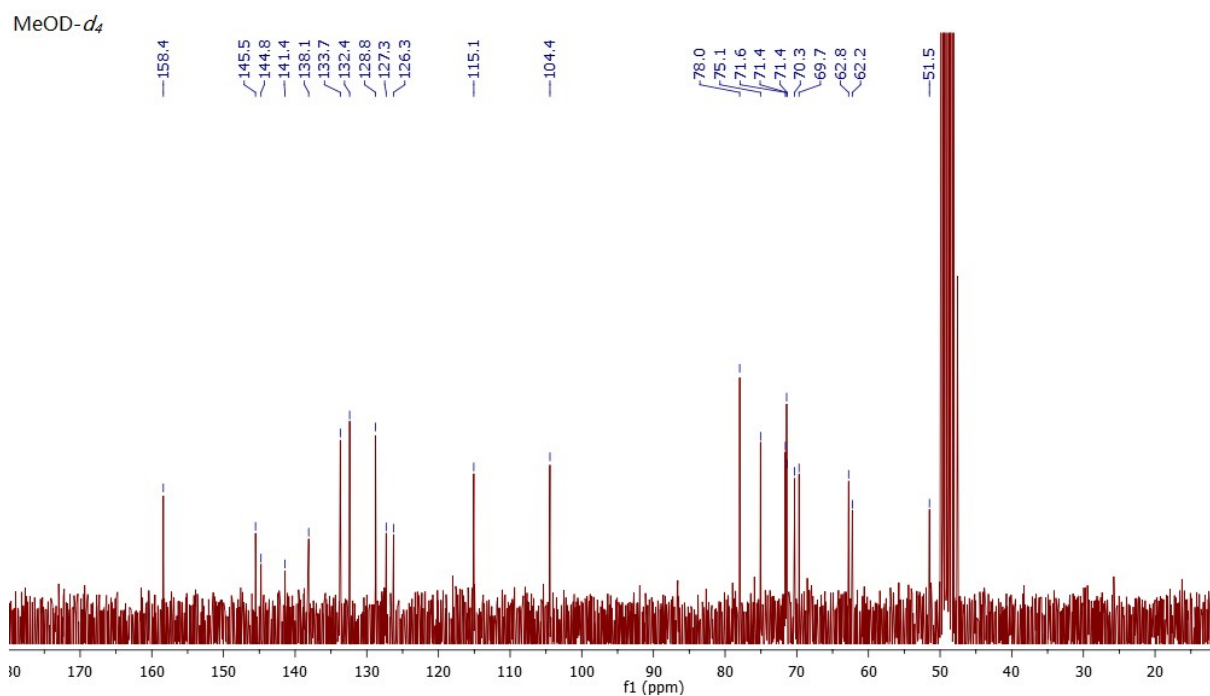
To a solution of compound **5** (1.05 g, 0.72 mmol) in methanol (15 mL) was added H₂O (5 mL) and triethylamine (4 mL). The resulting solution was stirred at RT under argon overnight. QuadraPure[®] resin (2 g) was added in the solution to remove the residual copper. The mixture was filtered after stirring 18 h at RT. The resin was washed with methanol (3 \times 30 mL). The solvent was evaporated to afford the pure compound **TPE2S** (774 mg, 96%) as a pale yellow amorphous solid.

¹H NMR (300 MHz, CD₃OD): δ (ppm) 3.18-3.29 (m, 8H, H-2, H-3, H-4, H-5), 3.54-3.66 (m, 14H, OCH₂, H-6'), 3.79-3.91 (Glc-OCH₂, OCH₂CH₂N, H-6), 4.24 (d, J = 7.8 Hz, 2H, H-1), 4.56 (t, J = 5.1 Hz, 4H, OCH₂CH₂N), 5.05 (s, 4H, OCH₂-triaz), 6.71 (d, J = 8.7 Hz, 4H, H-Ar), 6.89 (d, J = 8.7 Hz, 4H, H-Ar), 6.93-6.96 (m, 4H, Ph), 7.03-7.06 (m, 6H, Ph), 8.06 (s, 2H, H-triaz).

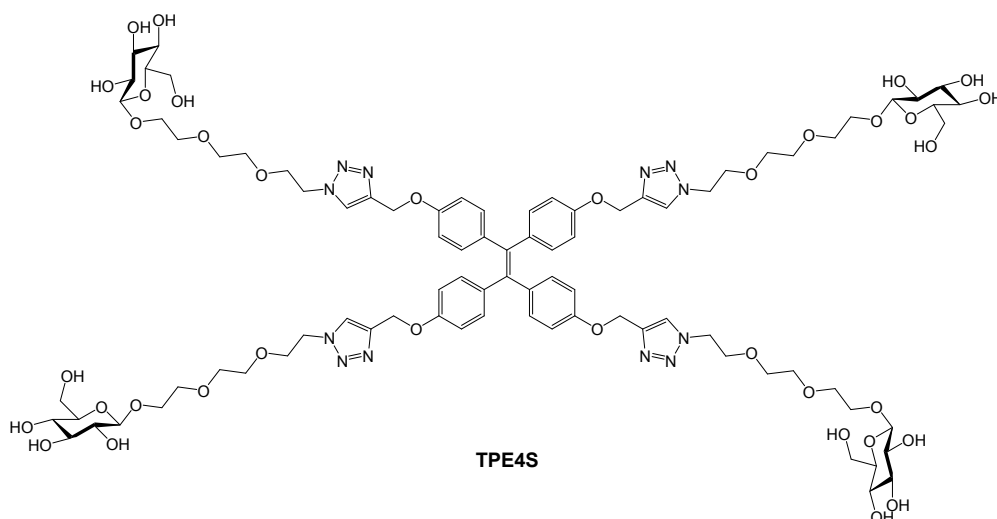
¹³C NMR (75 MHz, CD₃OD): δ (ppm) 51.5 (OCH₂CH₂N), 62.2 (C-6), 62.8 (OCH₂-triaz), 69.7 (Gal-OCH₂), 70.3 (OCH₂CH₂N), 71.35 (OCH₂), 71.41 (OCH₂), 71.43 (OCH₂), 71.6 (C-2), 75.1 (C-4), 77.9 (C-5), 78.0 (C-3), 104.4 (C-1), 115.1 (CH-Ar), 126.3 (CH^{triaz}), 127.3 (Ph), 128.8 (Ph), 132.4 (Ph), 133.7 (CH-Ar), 138.1 (C^{Ph}-C=C), 141.4 (C^{Ar}-C=C), 144.8 (C=C), 145.5 (C^{triaz}), 158.4 (C^{Ar}-O).

HR-ESI-MS m/z : calcd. for C₅₆H₇₀N₆O₁₈Na [M+Na]⁺ 1137.4645, found 1137.4644.





1,1,2,2-Tetrakis-(4{1-[1-(β-D-glucopyranosyloxy)-3,6-dioxaoct-8-yl]-1,2,3-triazol-4-ylmethoxy}phenyl)-ethylene (TPE4S):



The synthetic procedures of compound **TPE4S** were performed according to our reported previous work ^[2].

Experimental section for fluorescence measurements

General. The UV-vis absorbance measurements were carried out at room temperature by a Varian Cary 60 UV-vis spectrophotometer. All spectra were corrected for background intensities by subtracting the spectra of pure solvent measured under identical conditions. UV-vis-NIR absorption spectra (0-800 nm) of probes. The fluorescence measurements were carried out at room temperature by a JASCO Spectrofluorometer FP-8500. Ultrapure water was obtained from an ACCU 20 ULTRA PURE WATER unit.

Supramolecular self-assembly of glyco-dots. **TD-1** (1 mM, DMSO, 10 μ L) was added to a solution of TPE2S (1 mM, PBS, 0.01 M, pH 7.4, 950 μ L, and THF, 50 μ L). The resulting mixture was stirred at room temperature for 30 min in the dark to produce the supramolecular glyco-dots, which can be used as is.

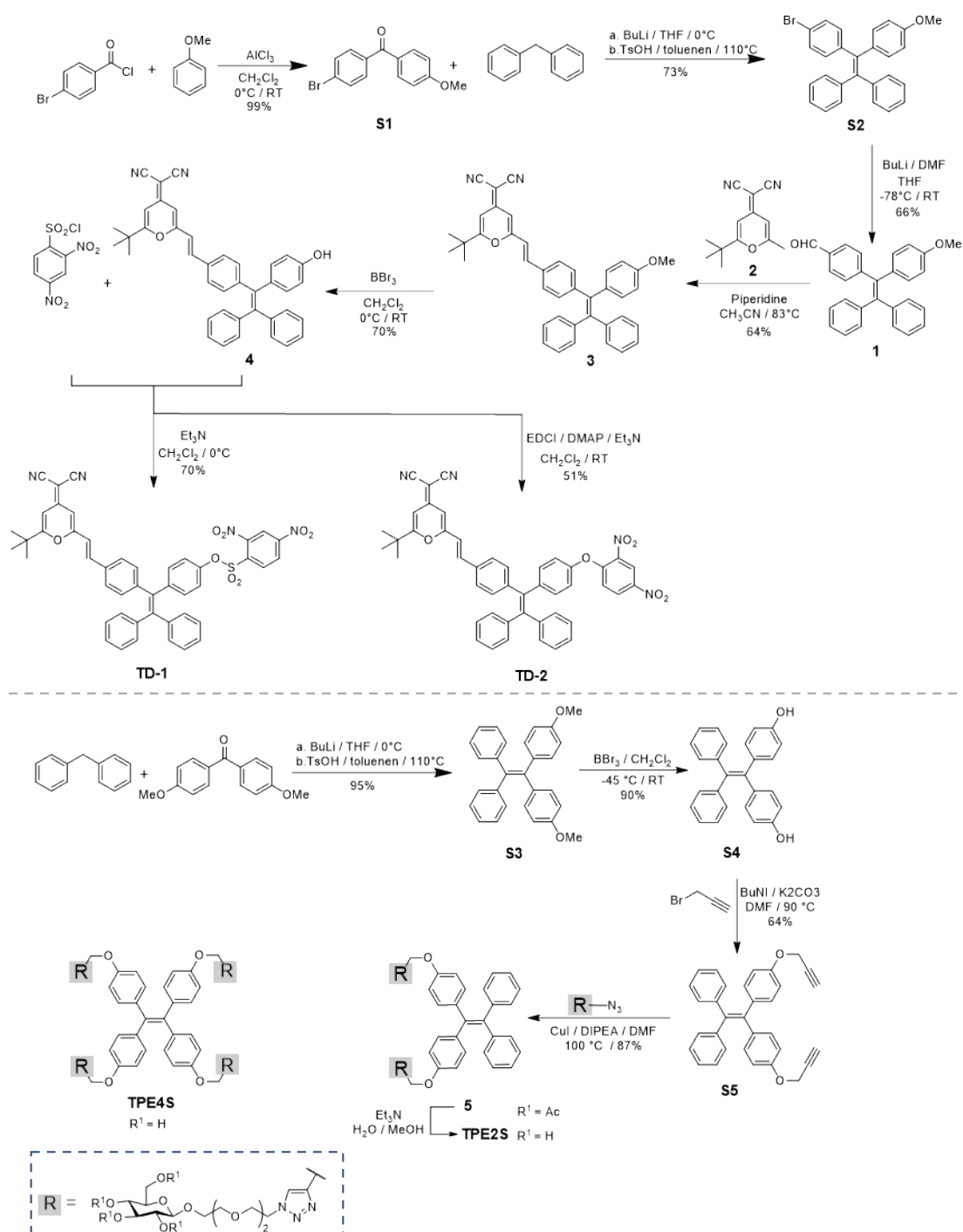
Fluorescence quantum yields. **TD-1** (with a final concentration of 10 μ M) was dissolved in aqueous solution (0.01 M, PBS, pH 7.4, 10% THF). **TD-1** (with a final concentration of 10 μ M) with addition of PhSH (with a final concentration of 100 μ M) was dissolved in aqueous solution (0.01 M, PBS, pH 7.4, 10% THF). Rhodamine B (with a final concentration of 5 μ M) was dissolved in aqueous solution (0.01 M, PBS, pH 7.4). The UV-vis absorbance measurements were carried out at room temperature by a Varian Cary 60 UV-vis spectrophotometer. Read the UV absorption values at 480/470 nm. The fluorescence measurements were carried out at room temperature by an Agilent Cary Eclipse fluorescence spectrophotometer with an excitation wavelength of 480/470 nm. Integrated fluorescence curve between 500 nm and 850 nm. Finally, the fluorescence quantum yield was calculated according to equation (1).

$$Y_u = Y_r \cdot \frac{F_u A_r n_u^2}{F_r A_u n_r^2} \quad (1)$$

u = probe, r = rhodamine B, Y means fluorescence quantum yield, F means integrated fluorescence intensity, A means absorbance, n means refractive index.

Dynamic light scattering. Dynamic light scattering was carried out using a Horiba LB-550 Dynamic Light Scattering Nano-Analyzer.

Additional figures and schemes



Scheme S1: Synthesis procedures of TPE-DCM based fluorescent probes and TPE-based glycoclusters.

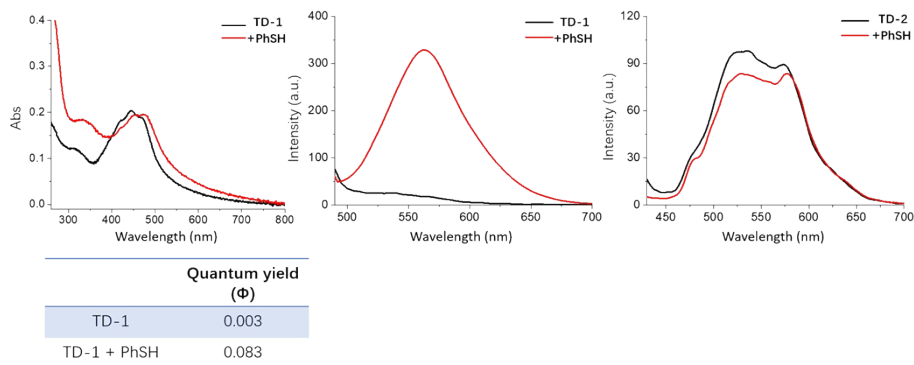


Figure S1: The absorption of TD-1 (left) and fluorescence emission changes upon excitation at 480 nm for TD-1 (middle) and excitation at 420 nm for TD-2 (right)

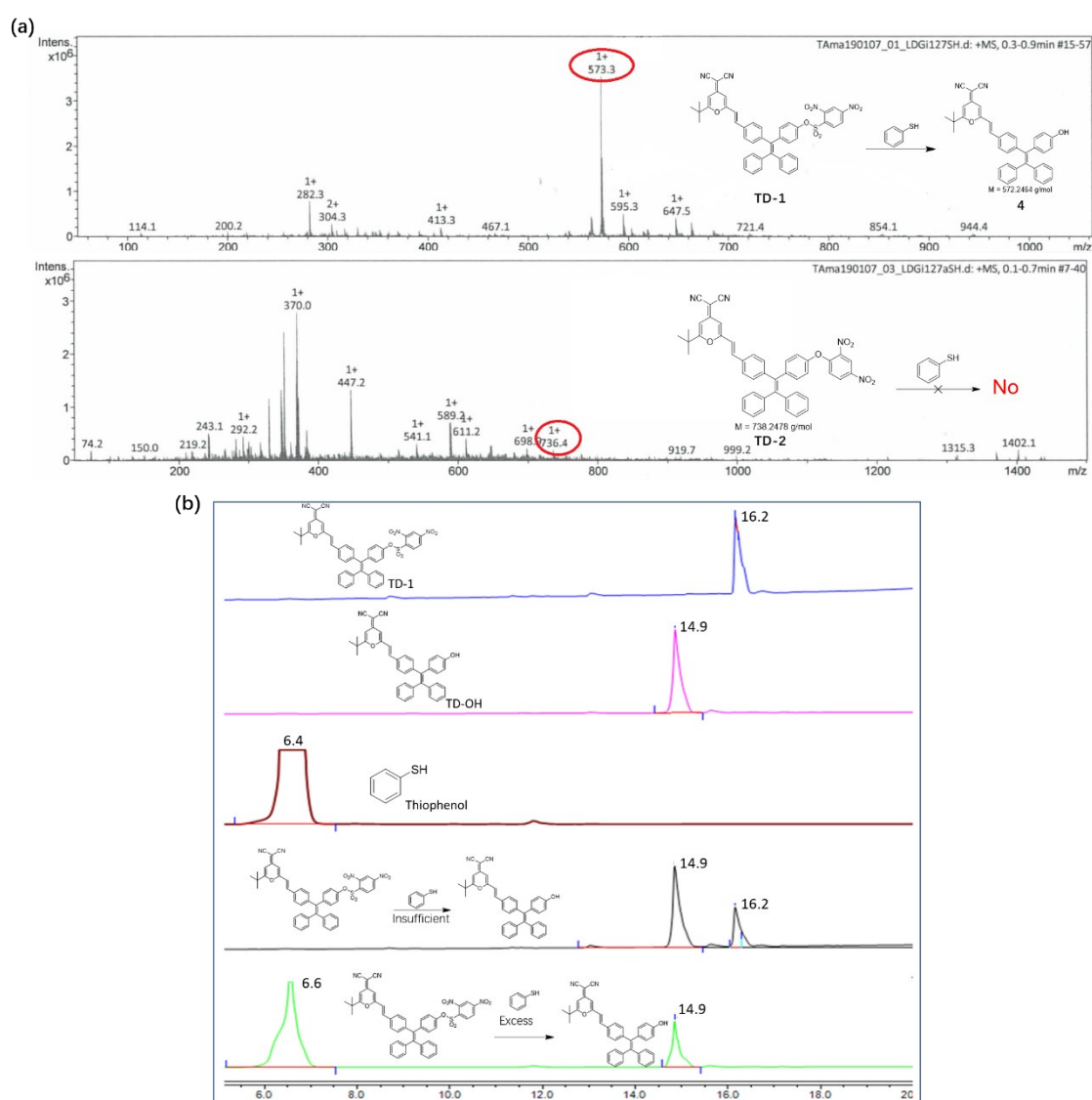


Figure S2: (a) Mass spectrometry and (b) HPLC analysis for the response mechanism of TD-1 for thiophenol detection. HPLC analysis was performed on UPLC Thermo Scientific Dionex UltiMate 3000 system equipped with a binary pump, an auto-sampler and a variable wavelength UV detector. The column for HPLC analysis was Thermo Scientific Accucore C8 80 Å, 2.1×50 mm, 2.6 μm using H₂O:MeCN = 1:0 to 0:1 during 20 min.

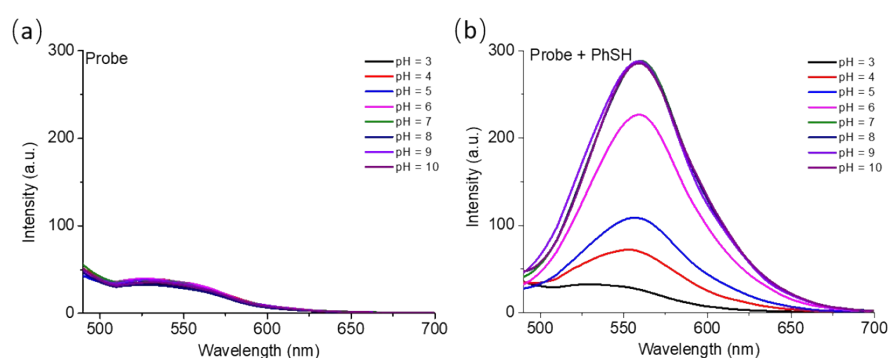


Figure S3: Fluorescence spectrum of TD-1 (10 μM) responding to thiophenol (100 μM) during 3 min in different pH PBS aqueous buffer (0.01 M) mixed with 10% THF. ($\lambda_{\text{ex}} = 480 \text{ nm}$)

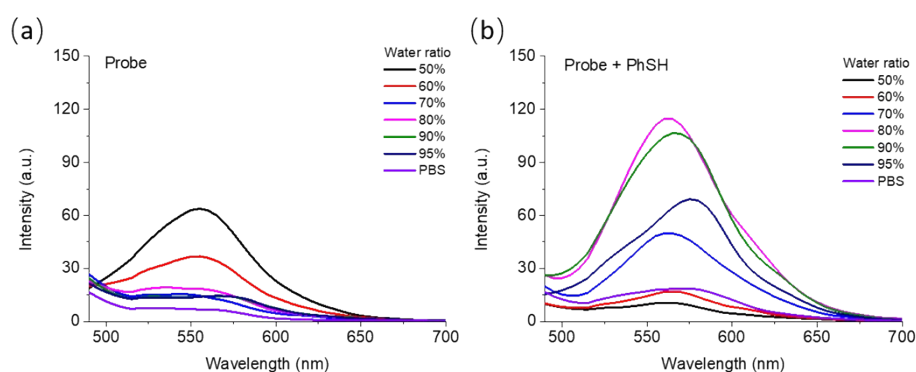


Figure S4: Fluorescence spectrum of TD-1 (10 μM) responding to thiophenol (100 μM) during 10 min with increasing the ratio of PBS buffer (0.01 M, pH = 7.3) in THF solution. ($\lambda_{\text{ex}} = 480 \text{ nm}$)

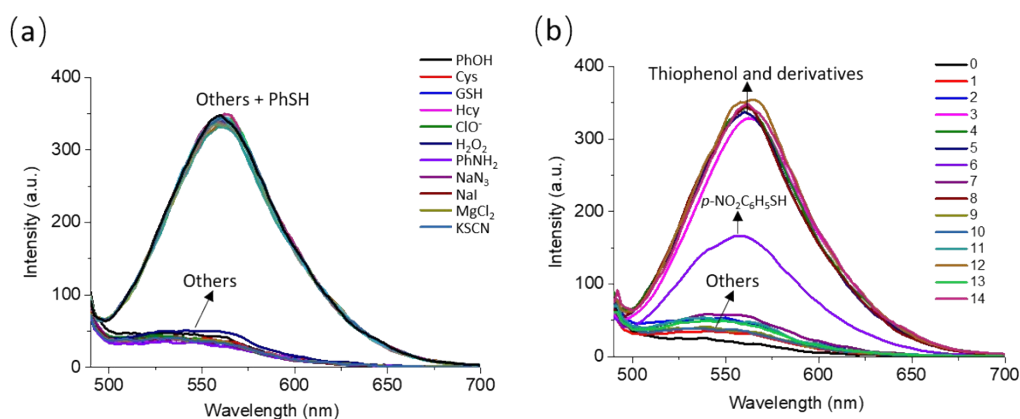


Figure S5: Fluorescence spectrum of TD-1 (10 μM) responding to (a) thiophenol (100 μM) with potential interfering species existance (50 μM), and detecting the (b) amphatic thiols, thiophenol and its derivatives during 3 min in PBS buffer (0.01 M, pH = 7.3) with 10% THF. Reagent: (0) Blank, (1) 1,2-ethanedithiol, (3) Cyclohexanethiol, (4) m-NH₂C₆H₅SH, (5) p-NH₂C₆H₅SH, (5) p-MeOC₆H₅SH, (6) p-NO₂C₆H₅SH, (7) p-CH₃C₆H₅SH, (8) 2-methyl-2-propanethiol, (9) pyrimidinethione, (10) α -thioglycerol, (11) 2-mercaptobenzo-thiazole, (12) 4,4'-thiobisbenzenethiol, (13) 2-aminoethanethiol hydrochloride, (14) C₆H₅SH. ($\lambda_{\text{ex}} = 480 \text{ nm}$)

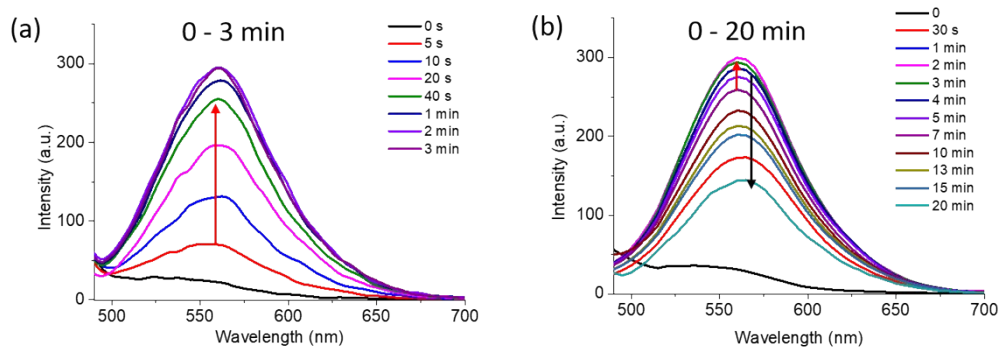


Figure S6: (a) Fluorescence intensity increase of TD-1 (10 μ M) incubating with thiophenol (100 μ M) during 3 min. (b) Fluorescence intensity decrease of TD-1 incubating with thiophenol after 3-20 min due to probe precipitation. ($\lambda_{ex} = 480$ nm)

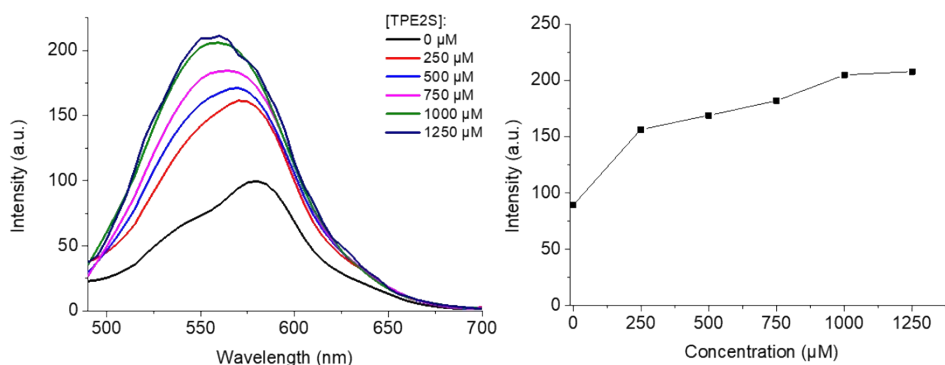


Figure S7: Fluorescence improvement of TD-1 (10 μ M) with addition of TPE2S (0-1250 μ M) in PBS buffer (pH 7.4, 0.01 M). ($\lambda_{ex} = 480$ nm)

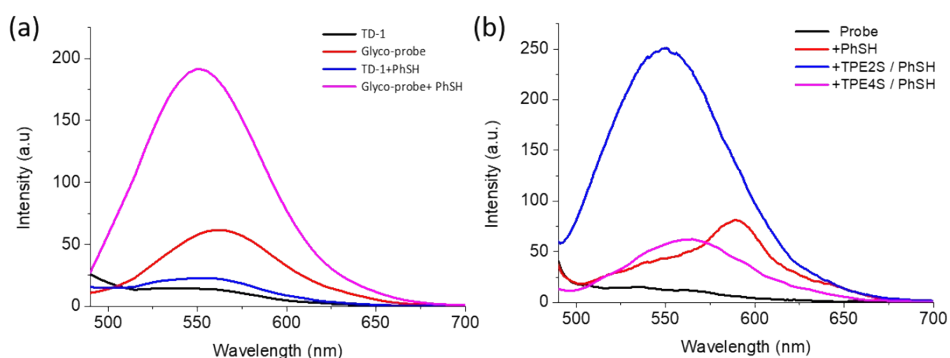


Figure S8: (a) Fluorescence changes of TD-1 (10 μ M) and glyco-probe after conjugation with TPE2S (10 mM) improved the fluorescence intensity for thiophenol (100 μ M) detection in 95% PBS (pH 7.3, 10 mM) with THF. (b) Fluorescence enhancement abilities of TPE2S and TPE4S (10 mM) conjugating TD-1 (10 μ M) and detect thiophenol (100 μ M) in PBS buffer (pH 7.3). ($\lambda_{ex} = 480$ nm)

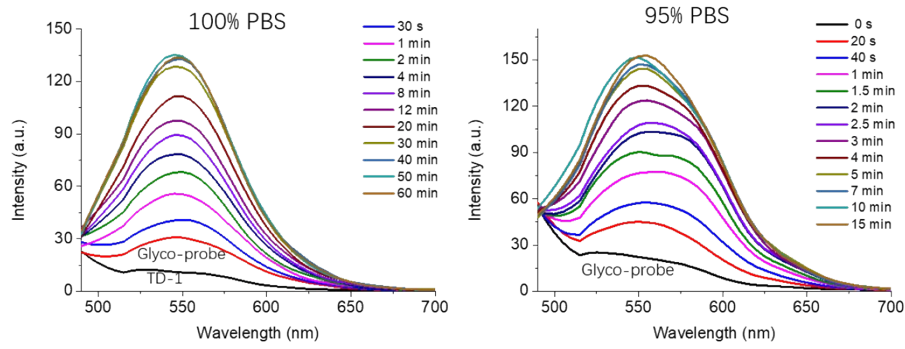


Figure S9: Glyco-probe responding to thiophenol ($100\ \mu\text{M}$) after self-assembling with TD-1 ($10\ \mu\text{M}$) and TPE2S ($10\ \text{mM}$) in 100% PBS buffer ($0.01\ \text{M}$, $\text{pH}=7.3$) or 95% PBS with THF. ($\lambda_{\text{ex}} = 480\ \text{nm}$)

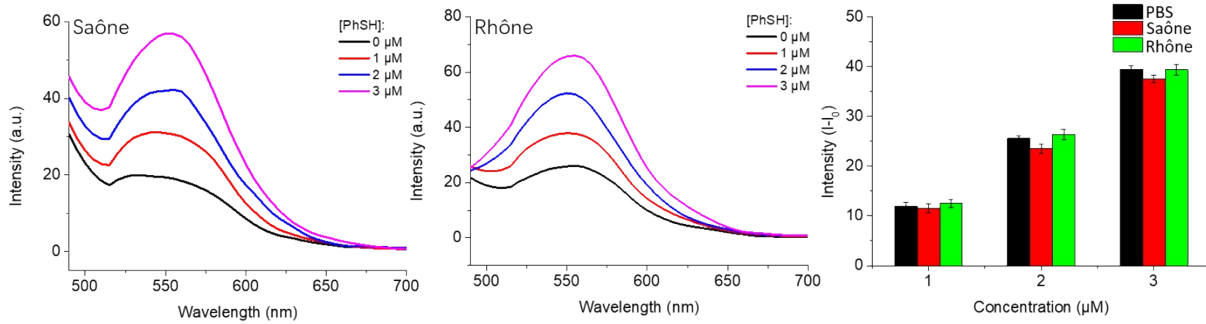


Figure S10: Glyco-probe quantifying thiophenol ($0\text{-}3\ \mu\text{M}$) after self-assembling with TD-1 ($10\ \mu\text{M}$) and TPE2S ($10\ \text{mM}$) in 95% real water samples from Saône River and Rhône River (Lyon, France). ($\lambda_{\text{ex}} = 480\ \text{nm}$)

References

- [1] G. Zhao, *et al.* Facile preparation and investigation of the properties of single molecular POSS-based white-light-emitting hybrid materials using click chemistry. *New Journal of Chemistry*, **2018**, *42*: 555-563.
- [2] M. Donnier-Marechal, *et al.* Tetraphenylethylene-based glycoclusters with aggregation-induced emission (AIE) properties as high-affinity ligands of bacterial lectins. *Org Biomol Chem*, **2018**, *16*: 8804-8809.