Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting information

Synthesis and Characterizations of Poly-3-((2,5-hydroquinone)vinyl)-1H-pyrrole: Investigation on Backbone/Pendant Interactions in a Conducting Redox Polymer

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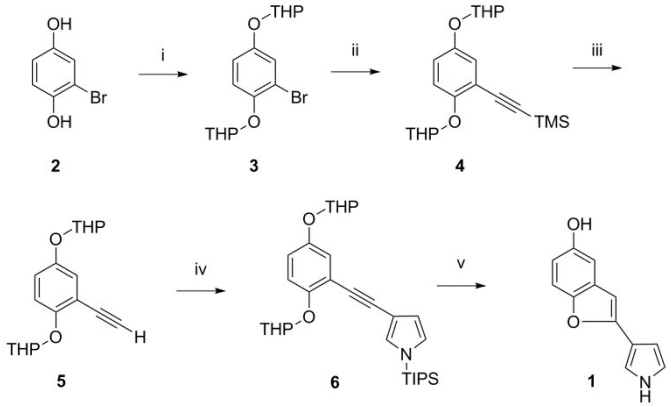
Monomer Synthesis

All reagents were purchased from Sigma Aldrich except boronic acid (purchased from Apollo Scientific Lt., purity was determined to be nearly 85%), and were used without further purification. All reactions were performed under argon atmosphere. Tetrahydrofuran (THF) was dried using a PureSolv PS-MD-4-EN solvent purification system and stored under argon atmosphere. Microwave reactions were performed in heavy-walled glass process vials sealed with aluminum crimp caps fitted with a silicon septum. The microwave heating was performed in a Biotage Initiator+ single-mode microwave cavity producing continuous irradiation at 2450 MHz. Flash chromatography was performed using either VWR Normasil 60 silica gel (40-63 μm, 60 Å) or on a Grace REVELERIS® X2 Flash Chromatography System using Reveleris® high resolution flash cartridges. Analytical thin layer chromatography was performed using pre-coated Merck Silica 60 F254 plates. Compound visualization was achieved with UV light (254 nm). High resolution NMR spectra were recorded on an Agilent 400-MR (^{1}H at 399.97 MHz, ^{13}C at 100.58 MHz) instrument. Chemical shifts are reported using the chloroform signal as an indirect reference to TMS (δ_H = 7.26 ppm, δ_C = 77.0 ppm). Coupling constants (*J*) are reported in Hz. Solid state NMR experiments were performed on a 14.1 T Agilent Inova (^{13}C and ^{1}H Larmor frequency of 150.9 and 600.1 MHz) equipped with a 3.2 mm double-resonance magic angle spinning (MAS) probe. ^{13}C cross polarization (CP) spectra were recorded at a spinning speed of 10 kHz using a CP time of 1 ms and a repetition delay of 15 s. 4096 signal accumulations were accumulated for each experiment. The ^{13}C chemical shift scale was referenced to solid adamantane. A moderate exponential function was applied to the free induction decay prior to Fourier transformation. IR spectra were recorded for neat compounds on a Perkin Elmer Spectrum 100 FT-IR spectrometer with UATR accessory. UV/vis spectra were recorded on a Shimadzu UV-1650PC spectrometer using 10 mm quartz cuvettes at room temperature (RT) with MeCN as solvent. (RT refers to 22 °C. High resolution mass spectra (HRMS) were acquired using a Thermo Scientific LTQ Orbitrap Velos apparatus in infusion mode. NMR and IR spectra are provided in the Supporting Information.



Scheme 1. Reaction conditions: i) Dihydropyran (DHP), trifluoroacetic acid (TFA), RT, overnight, 88 %; ii) ethynyltrimethylsilane, $Pd(PPh_3)Cl_2$, CuI, PPh_3, diethylamine, dimethylformamide (DMF), microwave heating at 120 °C, 1 h; iii) KOH (aq.), $CHCl_3$, MeOH, RT, 2 h, 72 %; iv) $Pd(PPh_3)_4$, CuI, Et_3N, MeCN, 100 °C, 3 h, 65 %; v) a: *p*-toluenesulfonic acid monohydrate, DCM, MeOH, RT, 4 h; b: TBAF, THF, AcOH, RT, 48 h, 71 %.

Bromo-2,5-bis((tetrahydro-2H-pyran-2-yl)oxy)benzene (3)

2-Bromo-1,4-hydroquinone **2** (105.82 mmol, 20.0 g) was dissolved in dihydropyran (DHP, 50 mL) at RT and 2-4 drops of trifluoroacetic acid (TFA) were added to the solution with continuous stirring. The mixture was kept stirring overnight. After the reaction was finished, the reaction mixture was diluted by adding 50 mL of diethyl

ether and then poured into an aqueous solution of NH_4Cl (50 mL). The aqueous layer was extracted with diethyl ether (3 ✕ 50 mL), dried over anhydrous $MgSO_4$, concentrated and purified by column chromatography, eluting with 10% ethyl acetate in n-pentane to afford product **3** as white solid (33.32 g, 88%, mixture of diastereomers). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.28 (dd, *J* = 2.9, 1 Hz, 1H), 7.06 (dd, *J* = 9.0, 1 Hz, 1H), 6.94 (dd, *J* = 9.0, 2.9 Hz, 1H), 5.36 (dd, *J* = 5.6, 3.1 Hz, 1H), 5.30 (dd, *J* = 5.6, 3.1 Hz, 1H), 3.92 (m, 2H), 3.60 (m, 2H), 2.08 (m, 1H), 1.96 (m, 2H), 1.86 (m, 3H), 1.67 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 152.22, 152.18, 148.37, 148.32, 121.53, 121.46, 117.87, 117.83, 116.55, 116.44, 113.49, 97.60, 97.54, 97.16, 97.10, 61.98, 61.85, 30.32, 30.25, 30.24, 25.26, 25.16, 18.68, 18.43. IR (neat): 2940, 2877, 1540 cm^{-1}; UV/vis (MeCN, λ_{max}): 237, 286 nm; HRMS (ESI; m / z, $[M + Na]^+$): Calcd for $C_{16}H_{21}BrNaO_4$, 379.0515; found, 379.0560.

2,5-Bis((tetrahydro-2H-pyran-2-yl)oxy)-(2-(trimethylsilyl)ethynyl)-benzene (4)
The THP-protected hydroquinone derivative **3** (2.60 mmol, 0.93 g), $CHCSiMe_3$ (3.10 mmol, 0.46 g), $Pd(PPh_3)_2Cl_2$ (0.13 mmol, 91 mg), CuI (0.13 mmol, 25 mg) and PPh_3 (0.52 mmol, 136 mg) were mixed in DMF (3 mL) in a microwave vial and degassed with argon bubbling for at least 5 min. Et_2NH (125.0 mmol, 9.14 g, 13 mL) was added, the vial was sealed and heated in the microwave cavity at 120 °C for 1 h. The resulting solution was extracted by adding 0.1 M HCl (15 mL) and then diethyl ether (3✕30 mL) and the organic layer was washed with aqueous $NaHCO_3$ solution. The separated organic layer was dried over anhydrous $MgSO_4$, concentrated, dissolved in n-pentane, passed through a celite pad and then the excess solvent was evaporated to give product **4** as a red oil (1.3 g, mixture of diastereomers) that solidified in the freezer. The crude product was used in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.13 (d, *J* = 2.9 Hz, 1H), 7.00 (dd, *J* = 1, 9.0 Hz, 1H), 6.95 (dd, *J* = 9.0, 2.9 Hz, 1H), 5.45 (m, 1H), 5.30 (m, 1H), 4.03 (m, 1H), 3.89 (m, 1H), 3.58 (m, 2H), 2.03 (m, 3H), 1.84 (m, 3H), 1.63 (m, 6H), 0.24 (s, 9H). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 152.98, 152.91, 151.54, 151.49, 121.01, 120.97, 118.70, 118.61, 117.86, 117.80, 114.89, 101.29, 98.07, 97.46, 97.36, 97.00, 96.93, 61.93, 61.64, 61.62, 30.37, 30.28, 30.26, 25.35, 25.21, 18.70, 18.27, 18.25, 0.0.; IR (neat): 2941, 2878, 2157, 1493 cm^{-1}; UV/vis (MeCN, λ_{max}): 245, 257, 306 nm; HRMS (ESI; m / z, $[M + Na]^+$): Calcd for $C_{21}H_{30}NaO_4Si$, 397.1811; found, 397.1837.

Ethynyl-2,5-bis((tetrahydro-2H-pyran-2-yl)oxy)benzene (5)
Compound **4** (5.20 g) was hydrolysed with 1M KOH (10 mL) solution, $CHCl_3$ (50 mL) and MeOH (70 mL) under stirring for 2 h at RT. The reaction mixture was extracted with $CHCl_3$ (3 ✕ 50 mL), dried over anhydrous $MgSO_4$, concentrated and purified by column chromatography, using 5% diethyl ether in pentane as eluent to give a colorless oil that solidified in the freezer as a white solid compound **5** (2.20 g, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.16 (d, *J* = 2.9 Hz, 1H), 7.03 (dd, *J* = 9.0, 1 Hz, 1H), 6.99 (dd, 2.9, 9.0 Hz, 1H), 5.42 (dd, *J* = 3.2, 6.5 Hz, 1H), 5.30 (dd, *J* = 5.4, 3.0 Hz, 1H), 4.93 (m, 2H), 3.59 (m, 2H), 3.22 (s, 1H), 2.00 (m, 3H), 1.85 (m, 3H), 1.64 (m, 6H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 153.08, 153.03, 151.42, 151.38, 121.57, 121.51, 118.87, 118.76, 117.38, 117.35, 113.50, 97.39, 97.32, 97.12, 97.05, 80.72, 80.00, 62.02, 62.01, 61.81, 61.80, 30.37, 30.36, 30.28, 30.26, 25.29, 25.18, 18.77, 18.76, 18.47, 18.45.; IR (neat): 3226, 2944, 2883, 1489 cm^{-1}; UV/vis (MeCN, λ_{max}): 247, 303, 310 nm; HRMS (ESI; m / z, $[M + H]^+$): Calcd for $C_{18}H_{23}O_4$, 303.1596; found, 303.1627.

3-(2-((2,5-bis((tetrahydro-2H-pyran-2-yl)oxy)phenyl))ethynyl)-1-(triisopropylsilyl)-1*H*-pyrrole (6)
Compound **5** (16.26 mmol, 4.92 g), 3-iodo-1-(triisopropylsilyl)-1*H*-pyrrole (16.26 mmol, 5.68 g), $Pd(PPh_3)_4$ and CuI (1.95 mmol, 0.37 g) were added to MeCN (70 mL) and Et_3N (140 mL) in a 500 mL round-bottom flask at RT under inert atmosphere. After heating to 100 °C for 3 h, the reaction was allowed to cool to RT. 0.1 M aqueous HCl (50 mL) solution was then added to the reaction mixture and the product was extracted with ethyl acetate (3 ✕ 150 mL). The separated organic layer was washed with aq. $NaHCO_3$ solution (2 ✕ 200 mL), dried over $MgSO_4$, concentrated and purified

by column chromatography with 10% diethyl ether in n-pentane to give crude **6** as a dense yellow liquid, which solidified in the freezer (5.54 g, 65%). The crude product was used in the next step without further purification.

2-(1H-pyrrol-3-yl)benzofuran-5-ol (1)
Compound **6** (3 g, 5.6 mmol) was dissolved in DCM (50 mL) and MeOH (50 mL), then p-toluenesulfonic acid monohydrate (150 mg, 0.79 mmol) was added. The mixture was stirred at RT for 4 h, and thereafter it was extracted with DCM (3 ✗ 50 mL). The combined organic phases were washed with water (3 ✗ 50 mL), then dried over anhydrous Na_2SO_4, concentrated and the solvent evaporated in high vacuum overnight. The resulting crude product was dissolved in THF (100 mL) and acetic acid (4.5 mL), followed by addition of a 1.0 M solution of TBAF in THF (14 mL). The reaction mixture was then stirred at RT overnight. After completed reaction, the mixture was poured into saturated aqueous NH_4Cl (50 mL) and extracted with ethyl acetate (3 ✗ 50 mL. The combined organic phases were washed with brine (3 ✗100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure yielding the crude product **1**. The crude product was purified on a silica column using 20 % ethyl acetate in n-pentane as eluent to give pure product as a slightly yellowsolid (0.8 g, 4 mmol, 71 %). ^{1}H NMR (400 MHz, CD_3OD) δ = 7.19 (m, 2H, Ph-H-3, Py-H-5), 6.84 (dd, *J* = 0.5, 2.3 Hz, 1H, Ph-H-6), 6.78 (dd, *J* = 2.8, 2.0 Hz, 1H, Py-H-4), 6.63 (dd, *J* = 2.8, 8.8 Hz, 1H, Ph-H-4), 6.51 (d, *J* = 1.1 Hz, 1H, CH=CH-1´), 6.47 (dd, *J* = 2.8, 1.5 Hz, 1H, Py-H-2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ = 156.9 (CH=CH-2´), 154.0 (Ph-5), 150 (Ph-2), 132.1 (Ph-1), 120 (Py-4), 117.0 (Py-5), 116.4 (Py-3), 112.0 (Ph-4), 111.3 (Ph-3), 106.6 (Py-2), 105.8 (Ph-6), 98.2 (CH=CH-1´); IR (neat): 3448, 3324, 3119, 2978, 1613 cm^{-1}; UV/vis (MeCN, λ_{max}): 240, 251, 273, 289, 317 nm; HRMS (ESI; m / z, $[M + H]^+$): Calcd for $C_{12}H_{10}NO_2$, 200.0712; found, 200.0731.

2. Spin density of monomers

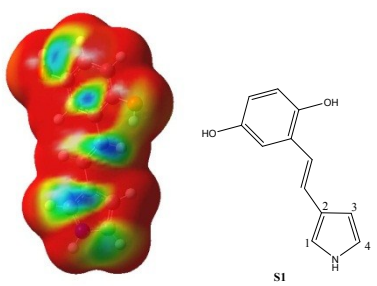


Figure S1. Calculated total electron density isosurface for *trans*-3-(2,5-dimethoxystyryl)-1*H*-pyrrole (**S1**) in the oxidized states, color mapped by spin density, from low (red) to high (blue) spin density.

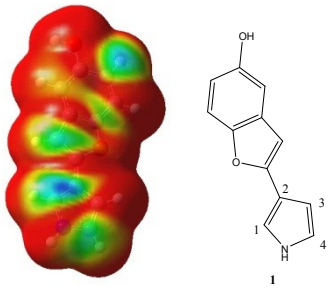


Figure S2. Calculated total electron density isosurface for 2-(1*H*-pyrrol-3-yl)benzofuran-5-ol (**1**) in the oxidized state, color mapped by spin density, from low (red) to high (blue) spin density.

For contrast, the color for carbon-1 on both isosurfaces was adjusted to be identical, therefore the color for spin density overall will change accordingly. As seen in figure **S1** and **S2**, there are more blue areas on **S1** despite the spin density on pyrrole ring looks quite close for both monomers. For better comparison of spin density on pyrrole, the spin density for each atom on the pyrrole ring is shown in table 1. Firstly, the spin density on carbon 1 and 4 in compound **1** is greater than those in compound **S1**. Secondly, the overall spin density on pyrrole ring in compound **1** is greater than that of compound **S1**. Both points imply the easier polymerizability on the pyrrole for compound **1** than compound **S1**.

Table 1. Spin density calculated by DFT for each atom on the pyrrole ring.

Atom	Spin density	
	1	S1
C-1	**0.206**	0.144
C-2	0.141	0.108
C-3	-0.067	-0.042
C-4	**0.125**	0.079
N	0.011	0.024
In total	0.415	0.314

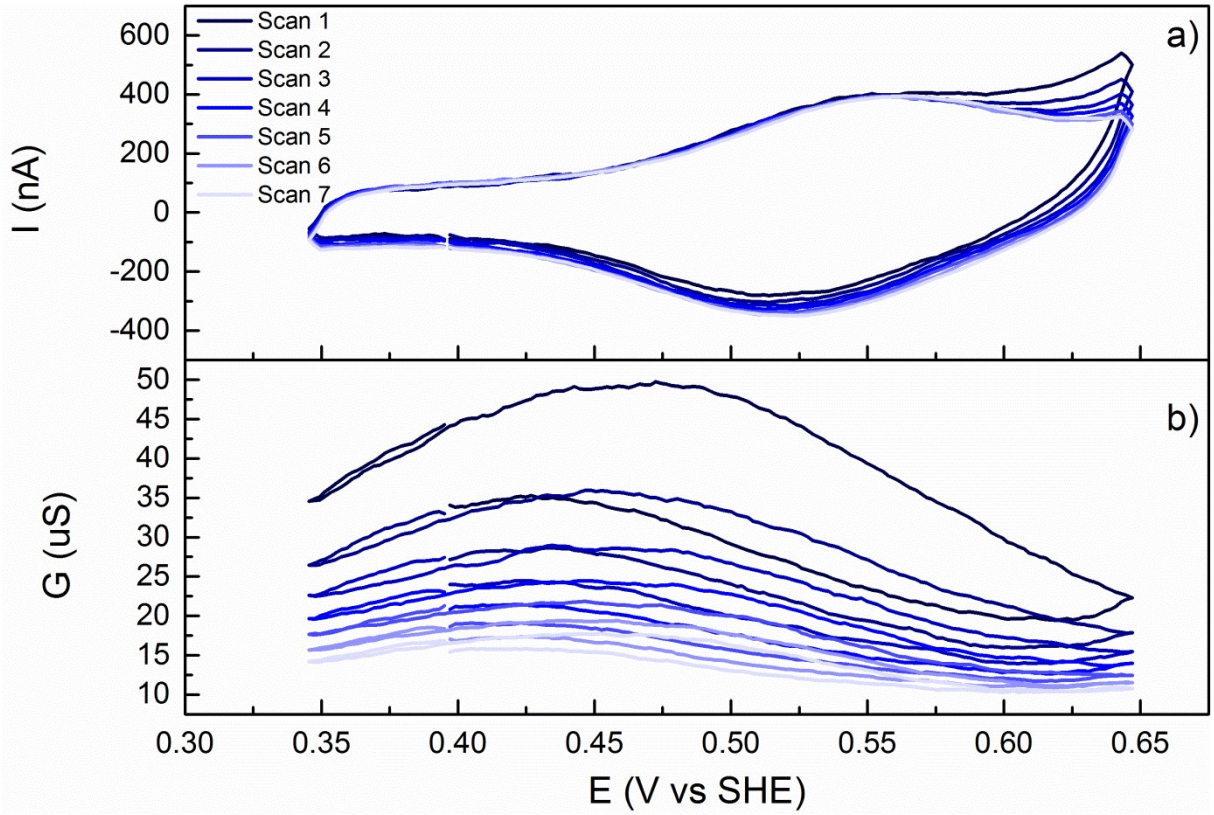


Figure S3. a) CV of **P1** grafted on IDA electrodes for consequent scans; b) In situ conductivity measurement of the polymer where a potential bias of 10 mV was applied between the WEs in aqueous electrolyte buffered with pH 2 during consequent scans.

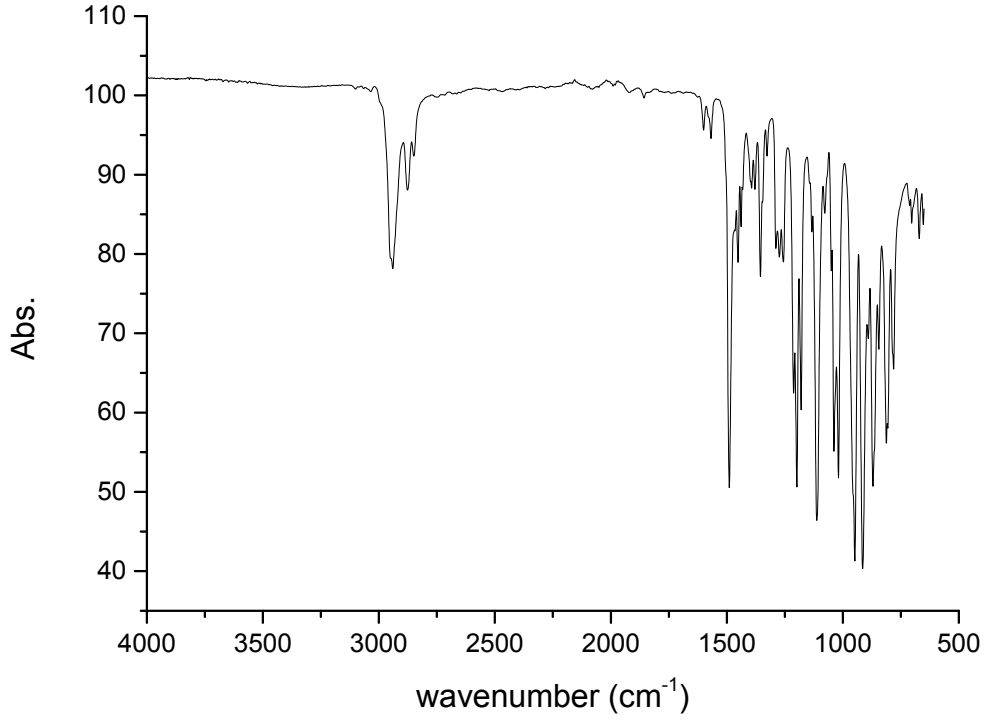


Figure S4. IR spectrum of compound **3**.

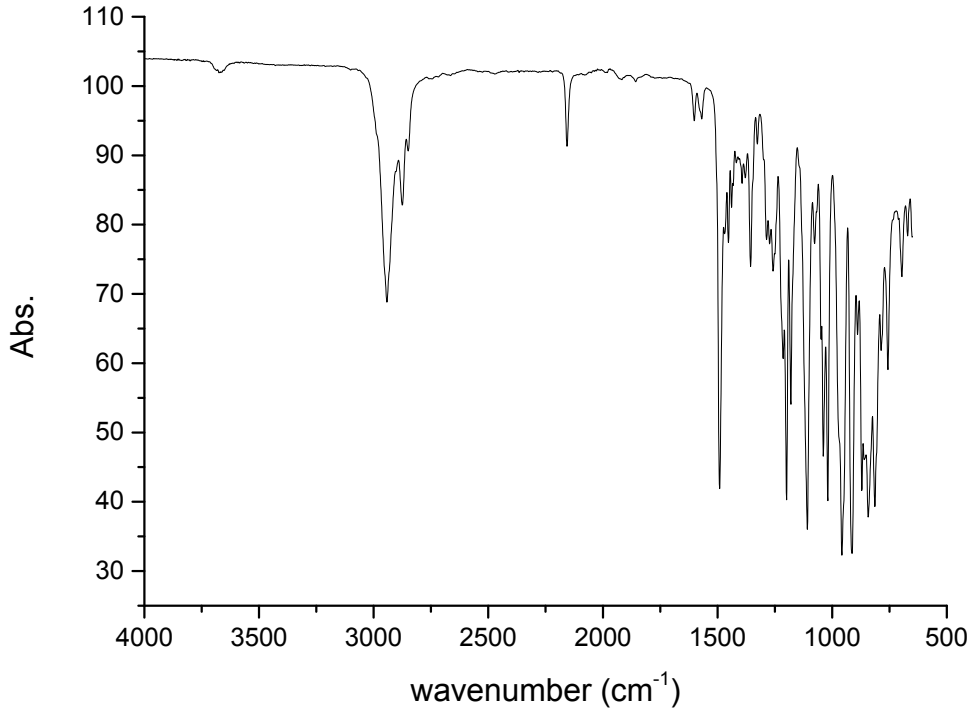


Figure S5. IR spectrum of compound **4**.

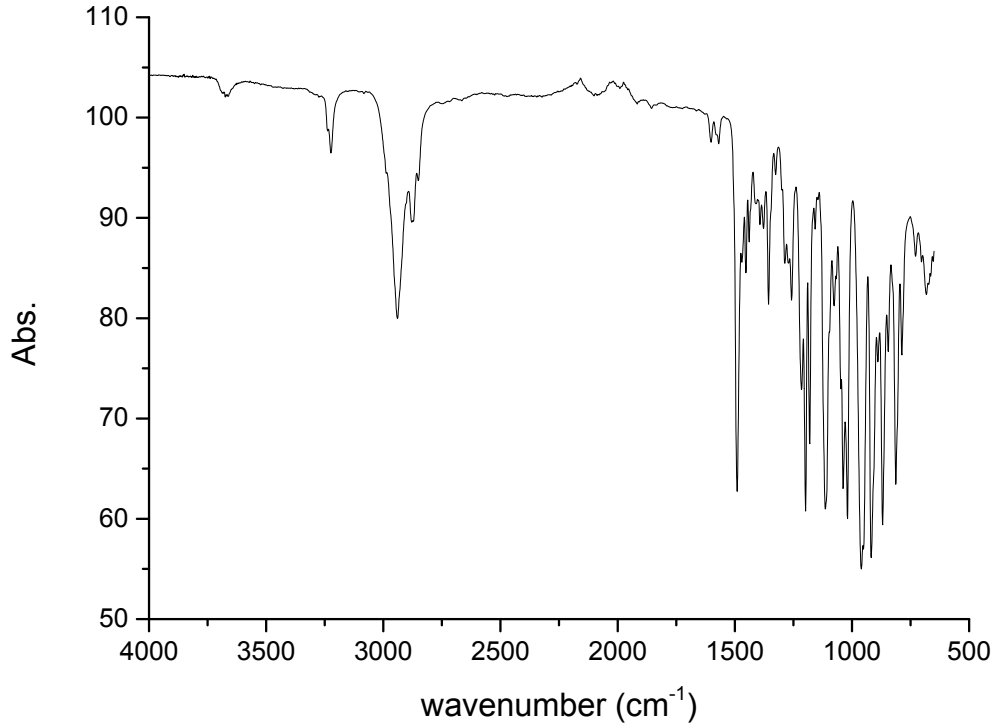


Figure S6. IR spectrum of compound **5**.

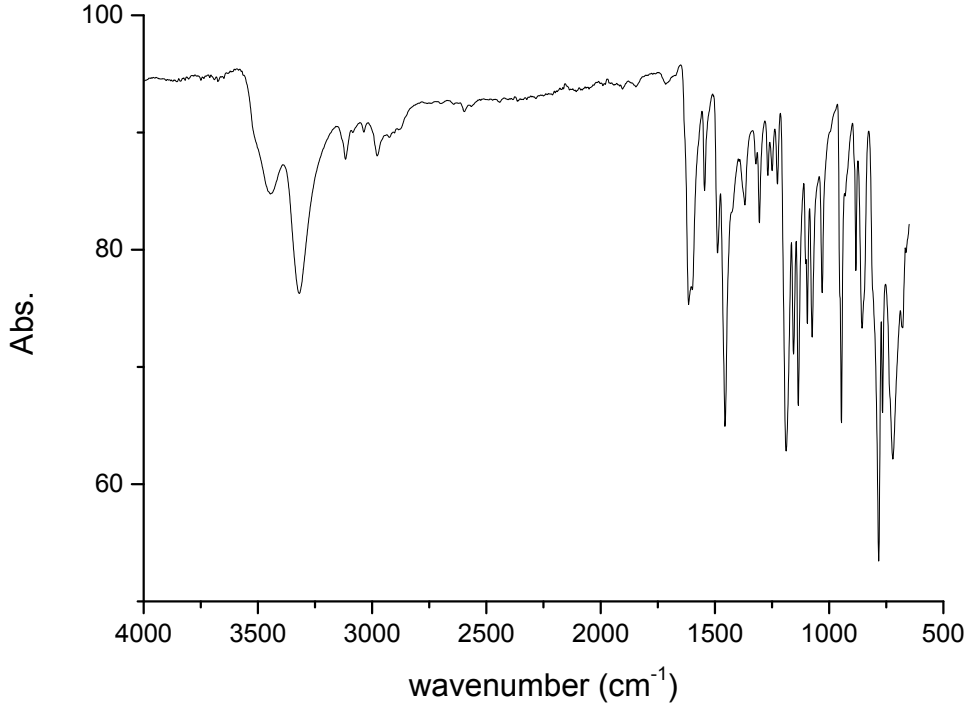


Figure S7. IR spectrum of compound **1**.

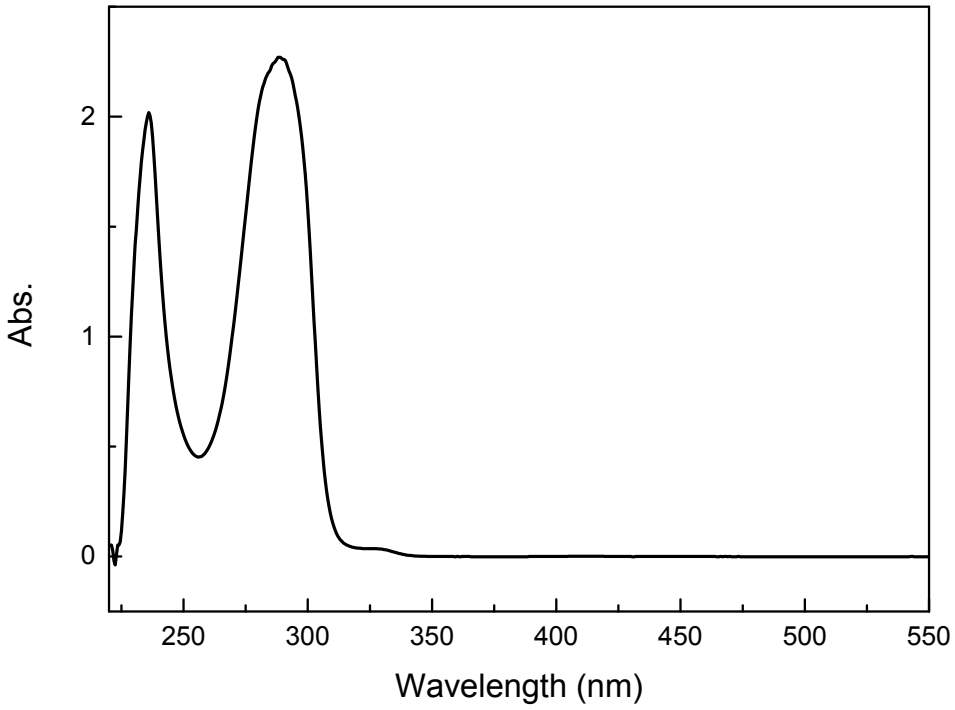


Figure S8. UV-vis spectrum of compound **3**.

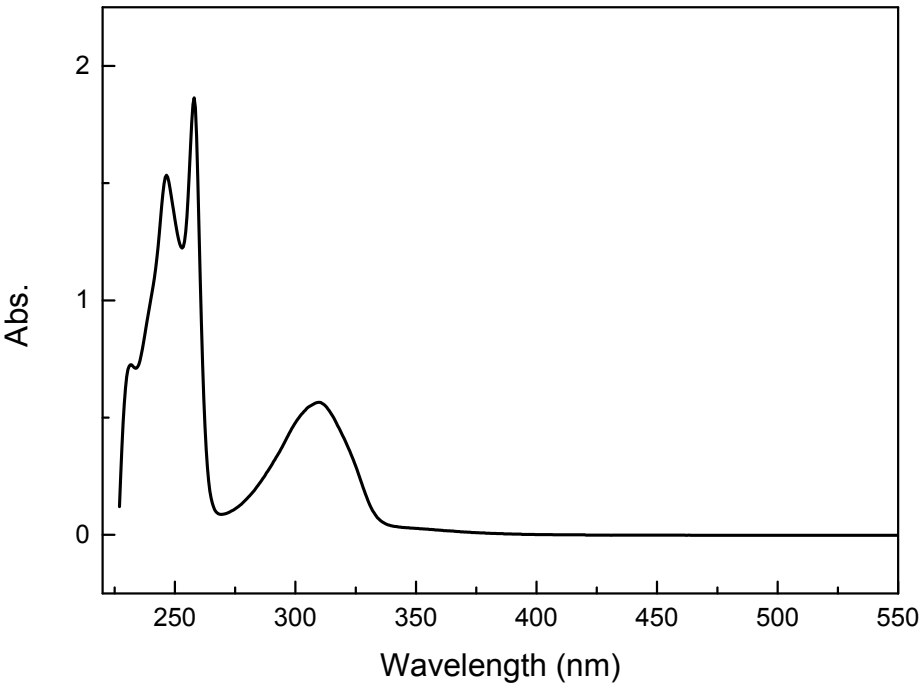


Figure S9. UV-vis spectrum of compound **4**.

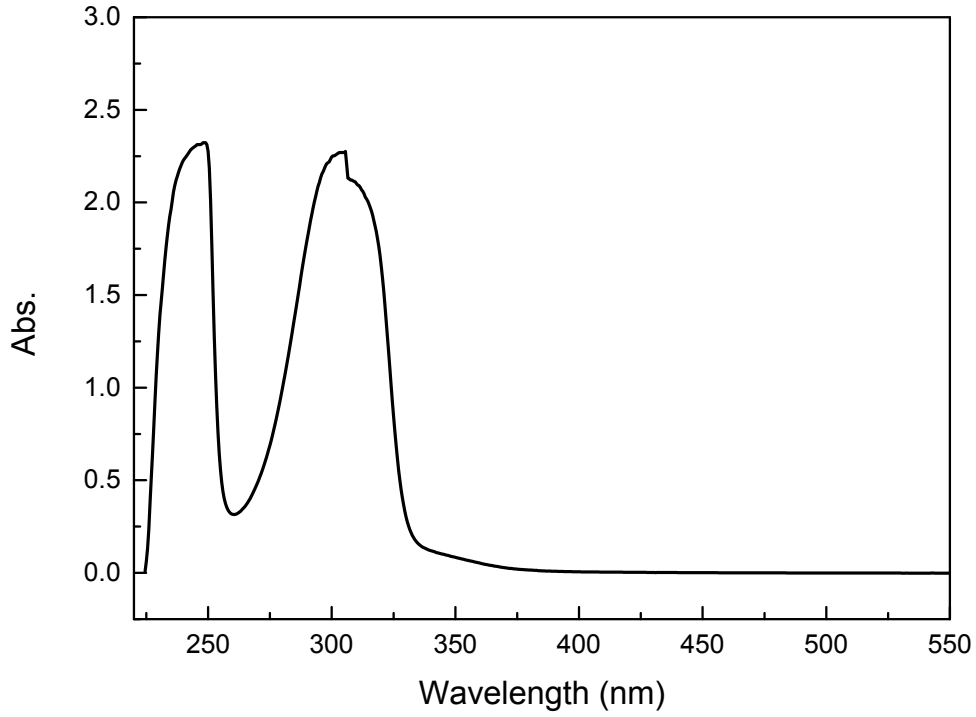


Figure S10. UV-vis spectrum of compound **5**.

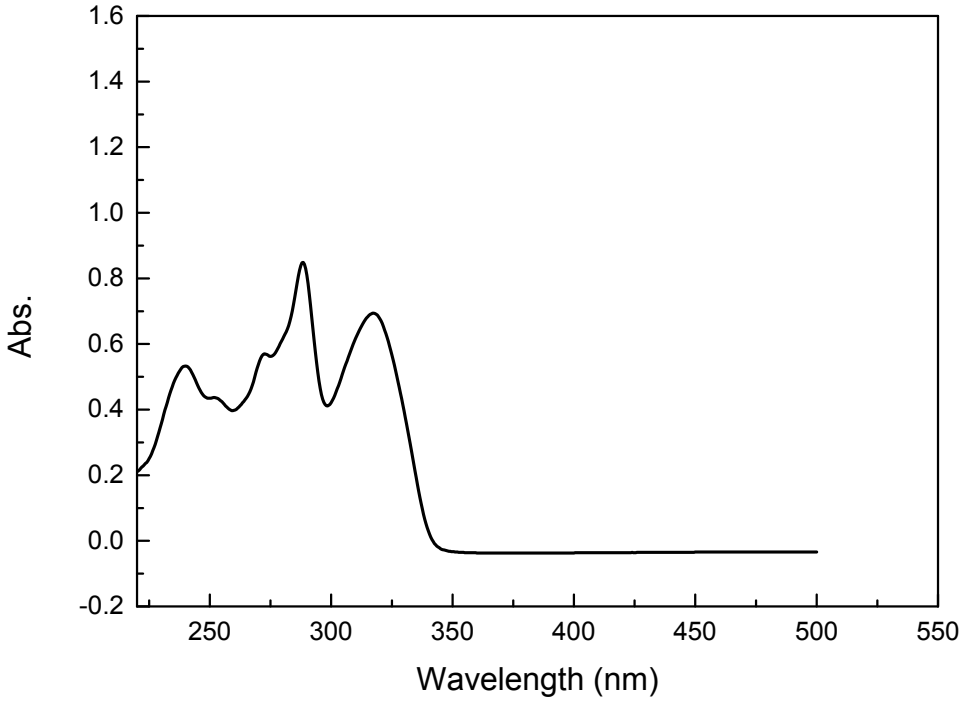


Figure S11. UV-vis spectrum of compound **1**.