Supplementary Information for

(*E*)-5,5′-Di(thiophen-2-yl)-3,3′-bi[thiophen-3(2*H*)-ylidene]-2,2′-diones—

From Conspicuous Blue Impurities to "Quasi-Metallic" Golden-Bronze Crystals

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1 Deconvolution of Ultraviolet–Visible Absorption Spectra

1.1 Introduction

1.1.1 Molar absorption coefficients and Gaussian functions

The molar absorption coefficient (ε) is a measure of how strongly a molecule absorbs electromagnetic radiation as a function of the frequency of the radiation. In the ultraviolet–visible spectrum the molar absorption coefficient is the sum of contributions from many electronic transitions ($\varepsilon_{m\leftarrow 0}$). These transitions are from the electronic ground state to the many electronic excited states:

$$\varepsilon = \sum_{m=1} \varepsilon_{m\leftarrow 0} \tag{S1}$$

ε Molar absorption coefficient of a particular molecule. (L cm^{-1} mol^{-1})

m Index of the (singlet) electronic states:

         $m = 0$ is the electronic ground state;

         $m = 1$ is the first electronic excited state; *etc*.

$\varepsilon_{m\leftarrow 0}$ Molar absorption coefficient for the transition from the electronic ground state to the electronic excited state m of a particular molecule. (L cm^{-1} mol^{-1})

In this work we are primarily interested in the transition to the first (singlet) electronic excited state. If this electronic transition is strongly coupled with a particular vibrational mode of the first electronic excited state then the corresponding molar absorption coefficient ($\varepsilon_{1\leftarrow 0}$) as a function of frequency will be the sum of a progression of peaks. Each successive peak after the first is the result of a transition to one of the vibrational excited states. The shapes of these peaks can be approximated by Gaussian functions (g_{n-0}):

$$\varepsilon_{1\leftarrow 0} \cong \sum_{n=0} g_{n-0} \tag{S2}$$

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$\varepsilon_{1\leftarrow0}$ Molar absorption coefficient for the transition from the electronic ground state to the first (singlet) electronic excited state of a particular molecule. ($L\ cm^{-1}\ mol^{-1}$)

n Index of the vibrational states of a particular vibrational mode of the first (singlet) electronic excited state:

    $n = 0$ is the vibrational ground state;

    $n = 1$ is the first vibrational excited state; *etc.*

g_{n-0} Gaussian function that approximates the molar absorption coefficient for the transition from the vibrational ground state of the electronic ground state to the vibrational (ground or excited) state n of the first (singlet) electronic excited state. ($L\ cm^{-1}\ mol^{-1}$)

The line shapes of the Gaussian functions (g_{n-0}) are adjusted to best fit the function $\varepsilon_{1\leftarrow0}$ by optimising the following parameters:

$$g_{n-0} = \varepsilon_{\max,n} \exp\left(-\frac{(\tilde{v} - \tilde{v}_{n-0})^2}{2\tilde{v}_{\text{width},n}^2}\right) \tag{S3}$$

$\varepsilon_{\max,n}$ Maximum value of the Gaussian function g_{n-0}. ($L\ cm^{-1}\ mol^{-1}$)

$\tilde{v}$ Frequency (wavenumber) of electromagnetic radiation. (cm^{-1})

$\tilde{v}_{n-0}$ Frequency (wavenumber) at which the maximum value of the Gaussian function g_{n-0} occurs. (cm^{-1})

$\tilde{v}_{\text{width},n}$ Parameter that is proportional to the peak width of the Gaussian function g_{n-0} as defined by the *full width at half maximum*, *etc.* (cm^{-1})

The number of peaks ($n + 1$) and the frequencies of the maxima can be difficult to determine if the function $\varepsilon_{1\leftarrow0}$ does not have a clear progression of maxima. When faced with this difficulty we can constrain our optimisation problem by assuming that the frequencies of the maxima ($\tilde{v}_{n-0}$) are evenly spaced (which should be quite a good approximation):

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$$\tilde{v}_{n-0} = \tilde{v}_{0-0} + n\,\tilde{v}_{vib} \tag{S4}$$

$\tilde{v}_{0-0}$ Frequency (wavenumber) at which the maximum value of the Gaussian function g_{0-0} occurs. (cm^{-1})

$\tilde{v}_{vib}$ Frequency (wavenumber) of the particular vibrational mode of the first (singlet) electronic excited state that is strongly coupled with the transition from the electronic ground state to the first (singlet) electronic excited state. (cm^{-1})

1.1.2 Comparing transition intensities

Sometimes we want to compare the intensities of different transitions, *e.g.* different electronic or vibrational transitions of a particular molecule; similar electronic transitions of different molecules; *etc*. If we want to compare the intensities at a particular frequency we can compare the molar absorption coefficients at that frequency. Alternatively we can make our comparison independent of frequency. We achieve this by comparing the integrals over all frequencies of the molar absorption coefficients.

To compare the intensities of transitions from the electronic ground state to the first (singlet) electronic excited state of different molecules, independently of frequency, we compare the integrals over all frequencies ($\tilde{v}$) of the corresponding molar absorption coefficients ($\varepsilon_{1\leftarrow0}$). These integrals are approximated by the sum of the integrals of the corresponding (fitted) Gaussian functions (g_{n-0}): (Integral of eq S2)

$$\int_{-\infty}^{+\infty} \varepsilon_{1\leftarrow0}\, d\tilde{v} \cong \sum_{n=0} \int_{-\infty}^{+\infty} g_{n-0}\, d\tilde{v} \tag{S5}$$

The integrals over all frequencies ($\tilde{v}$) of our Gaussian functions (g_{n-0}) are easy to calculate (if we don't mind including negative frequencies for mathematical convenience as opposed to any physical reality): (Integral of eq S3)

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$$\int_{-\infty}^{+\infty} g_{n-0} \, d\tilde{\nu} = \sqrt{2\pi} \varepsilon_{\text{max},n} \tilde{\nu}_{\text{width},n} \tag{S6}$$

1.1.3 Oscillator strengths

The oscillator strength is a standard way of comparing the calculated and experimentally determined intensities of transitions. The oscillator strength of a transition from the electronic ground state to the first (singlet) electronic excited state of a particular molecule ($f_{1\leftarrow 0}$) is the ratio:[1]

$$f_{1\leftarrow 0} = \frac{\int_{-\infty}^{+\infty} \sigma_{1\leftarrow 0} \, d\omega}{\int_{-\infty}^{+\infty} \sigma_{\text{c}} \, d\omega} \tag{S7}$$

$f_{1\leftarrow 0}$ Oscillator strength of the transition from the electronic ground state to the first (singlet) electronic excited state of a particular molecule. (dimensionless)

$\sigma_{1\leftarrow 0}$ Absorption cross section of the transition from the electronic ground state to the first (singlet) electronic excited state of a particular molecule. (m^2)

σ_{c} Absorption cross section of a classical electron formulated as a one-dimensional harmonic oscillator, damped by the emission of radiation and driven by a sinusoidal electric field with frequency ω. (m^2)

ω Frequency (angular frequency) of electromagnetic radiation. (rad s^{-1})

The integral over all frequencies (ω) of the absorption cross section of a classical electron (σ_{c}) is:[1]

$$\int_{-\infty}^{+\infty} \sigma_{\text{c}} \, d\omega = \frac{\pi e^2}{2c\varepsilon_0 m_{\text{e}}} \tag{S8}$$

e Elementary charge. (1.602×10^{-19} C)

c Speed of light in vacuum. (2.998×10^8 m s^{-1})

ε_0 Vacuum permittivity. (8.854×10^{-12} C^2 s^2 kg^{-1} m^{-3})

m_{e} Mass of an electron. (9.109×10^{-31} kg)

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The absorption cross section (σ) is merely another measure of how strongly a molecule absorbs electromagnetic radiation as a function of the frequency of the radiation:

$$\ln\left(\frac{I_0}{I}\right) = \sigma N_A c_M l \tag{S9}$$

I_0 Intensity of incident electromagnetic radiation. ($\text{J m}^{-2}\,\text{s}^{-1}$)

I Intensity of transmitted electromagnetic radiation. ($\text{J m}^{-2}\,\text{s}^{-1}$)

σ Absorption cross section of a particular molecule. (m^2)

N_A Avogadro constant. ($6.022 \times 10^{23}\ \text{mol}^{-1}$)

c_M Concentration of a particular molecule. (mol m^{-3} in this equation)

l Path length through the concentration of molecules. (m in this equation)

We can write the equation for the oscillator strength in terms of our familiar experimental measurements and units by relating the absorption cross section to the molar absorption coefficient and angular frequency to wavenumber. The definition of the absorption cross section is similar to that of the molar absorption coefficient (ε):

$$\log_{10}\left(\frac{I_0}{I}\right) = \varepsilon c_M l \tag{S10}$$

ε Molar absorption coefficient of a particular molecule. ($\text{L cm}^{-1}\,\text{mol}^{-1}$)

c_M Concentration of a particular molecule. (mol L^{-1} in this equation)

l Path length through the concentration of molecules. (cm in this equation)

The absorption cross section (σ) is proportional to the molar absorption coefficient (ε): (Combining eq S9 and S10)

$$\sigma = \ln(10)\,\frac{\varepsilon}{N_A}\,\frac{\text{cm m}^2}{10\ \text{L}} \tag{S11}$$

Angular frequency (ω) is proportional to wavenumber ($\tilde{\nu}$):

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$$\omega = 2\pi c \tilde{v} \frac{100 \text{ cm}}{\text{m}} \tag{S12}$$

ω Frequency (angular frequency) of electromagnetic radiation. (rad s^{-1})

$\tilde{v}$ Frequency (wavenumber) of electromagnetic radiation. (cm^{-1})

We can now see that the oscillator strength of a transition from the electronic ground state to the first (singlet) electronic excited state of a particular molecule ($f_{1\leftarrow 0}$) is proportional to the integral over all frequencies ($\tilde{v}$) of the corresponding molar absorption coefficient ($\varepsilon_{1\leftarrow 0}$): (Combining eq S1, S7, S8, S11 and S12)

$$f_{1\leftarrow 0} = \ln(10) \frac{4c^2\varepsilon_0 m_e}{e^2 N_A} \frac{10 \text{ cm}^2 \text{ m}}{\text{L}} \int_{-\infty}^{+\infty} \varepsilon_{1\leftarrow 0} \, d\tilde{v} \tag{S13}$$

We can calculate the oscillator strength ($f_{1\leftarrow 0}$) from the sum of the integrals of the corresponding (fitted) Gaussian functions: (Combining eq S5, S6 and S13)

$$f_{1\leftarrow 0} \cong \ln(10) \sqrt{2\pi} \frac{4c^2\varepsilon_0 m_e}{e^2 N_A} \frac{10 \text{ cm}^2 \text{ m}}{\text{L}} \sum_{n=0} \varepsilon_{\max,n} \tilde{v}_{\text{width},n} \tag{S14}$$

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1.2 Deconvolution of the visible absorption spectra of the blue dyes (1)

The results of deconvoluting the visible absorption spectra of the blue dyes (**1**) are presented in Figure S1 and Table S1. Deconvolution was performed over intervals of wavenumbers where we were confident that only the transition from the ground electronic state to the first (singlet) electronic excited state significantly contributed to the absorption. The results were very similar whether three or four Gaussian functions were used. The sums of the Gaussian functions were fitted to the experimentally determined molar absorption coefficients by the method of least squares.
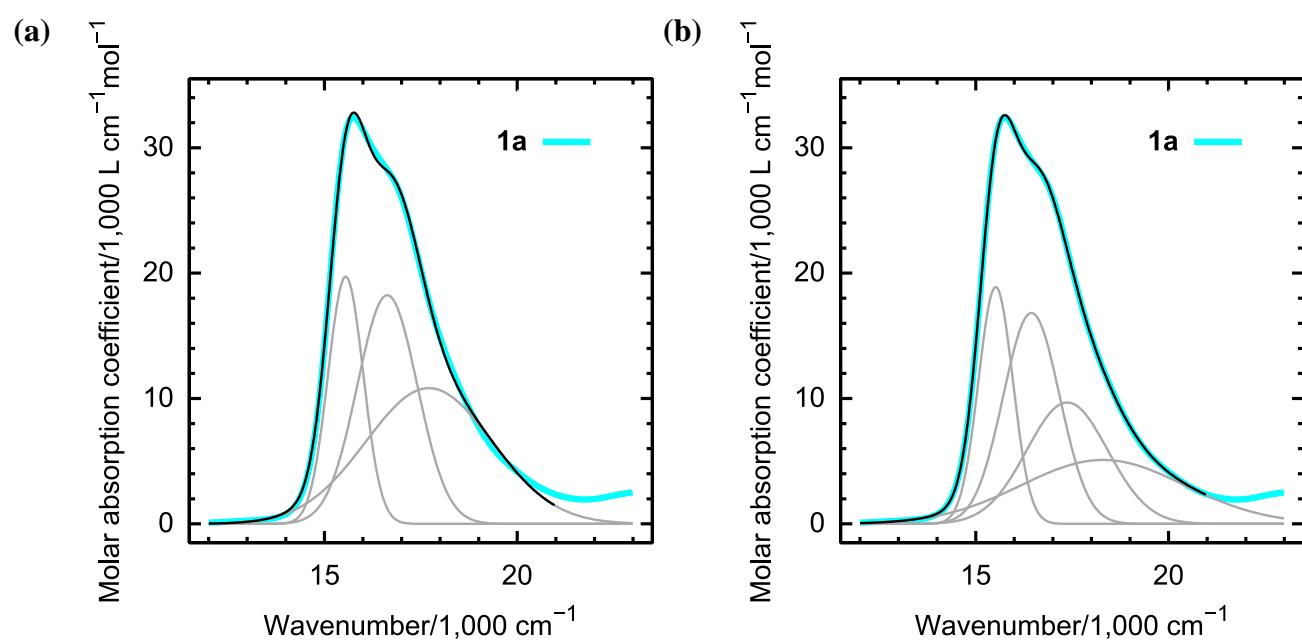
Figure S1. Deconvoluted visible absorption spectra of the blue dyes (**1**) in chloroform solutions. Transitions shown for each dye are those from the electronic ground state to the vibrational ground and excited states of the first (singlet) electronic excited state. Coloured curves are the experimentally determined molar absorption coefficients. Grey curves are Gaussian functions. Black curves are the sums of the Gaussian functions. The sums have been fitted to the experimental data over the intervals of wavenumbers indicated by the black curves. Deconvolution of absorption of **1a** with (a) three and (b) four Gaussian functions. *Figure continues on the next page.*

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

(c)

(d)

(e)

(f)
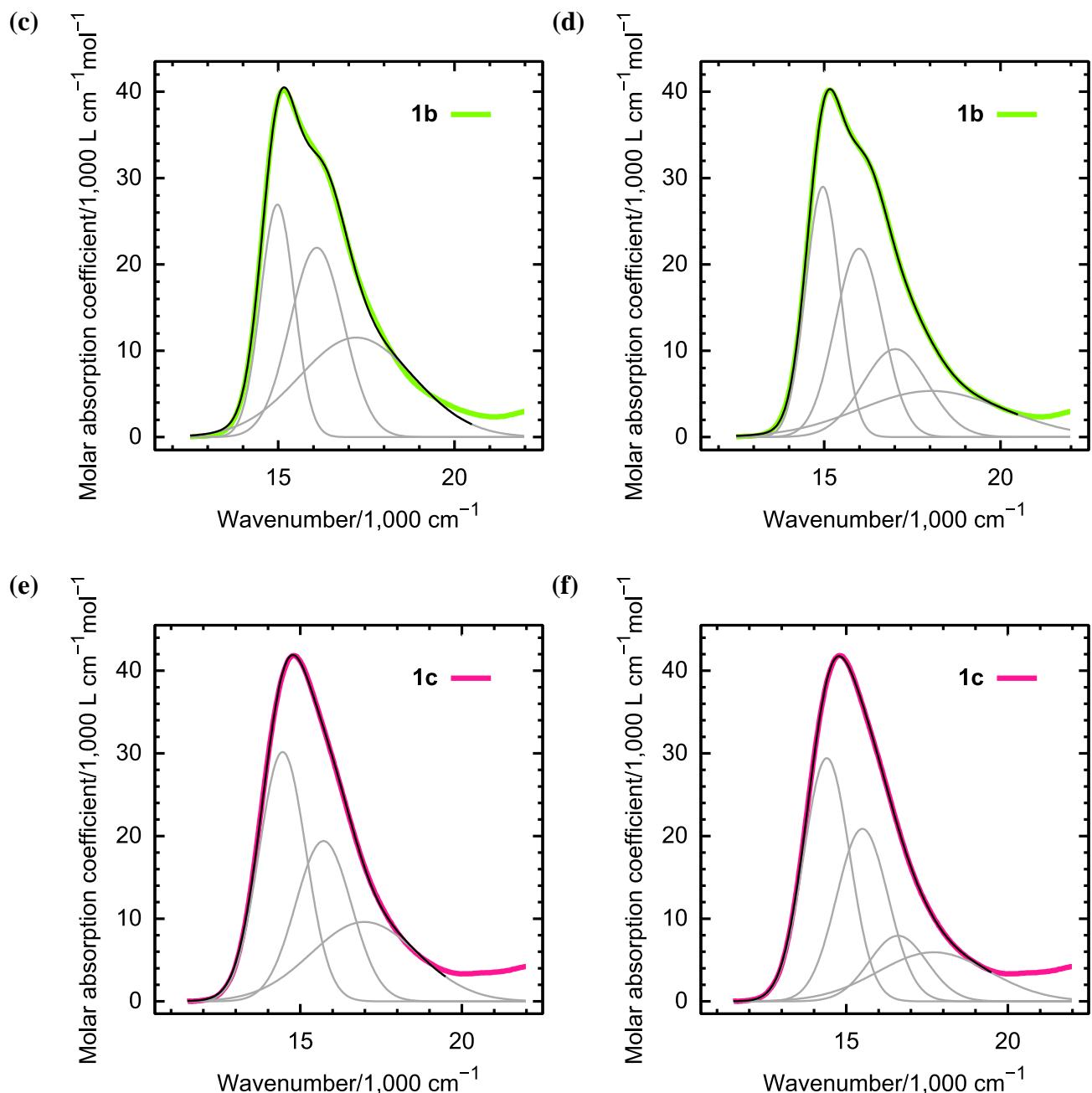
Figure S1 *continued from the previous page.* Deconvolution of absorption of **1b** with (c) three and (d) four Gaussian functions. Deconvolution of absorption of **1c** with (e) three and (f) four Gaussian functions.

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Table S1. Data from the Deconvolution of the Visible Absorption Spectra of the Blue Dyes (1).[a]

| Dye		1a		1b		1c	
Fitted interval of $\tilde{\nu}$/cm^{-1}		12,000–21,000		12,500–20,500		11,500–19,500	
Number of Gaussian functions[b]		3	4	3	4	3	4
$\tilde{\nu}_{0-0}$/cm^{-1} [c]		15,600	**15,500**	15,000	**15,000**	14,500	**14,400**
$\tilde{\nu}_{vib}$/cm^{-1} [c,d]		1,080	927	1,120	1,030	1,270	1,100
	$n = 0$	19,700	18,900	26,900	29,000	30,200	29,400
$\varepsilon_{max,n}$ [e]	$n = 1$	18,200	16,800	21,900	21,800	19,400	20,900
/L cm^{-1} mol^{-1}	$n = 2$	10,800	9,680	11,500	10,200	9,610	7,940
	$n = 3$	n/a	5,100	n/a	5,340	n/a	5,940
	$n = 0$	457	445	478	483	724	709
	$n = 1$	776	730	761	677	863	799
$\tilde{\nu}_{width,n}$/cm^{-1} [e]	$n = 2$	1,630	1,050	1,620	928	1,650	894
	$n = 3$	n/a	2,110	n/a	2,040	n/a	1,720
$f_{1\leftarrow 0}$ [f]		0.44	**0.45**	0.52	**0.53**	0.59	**0.59**

a Chloroform solutions. Data in boldface appear in Table 1 of the main article. *b* $b = n + 1$ (Eq S2). *c* Eq S4. *d* Wavenumbers of 1000–1300 cm^{-1} are typical for aryl C−H in-plane bends.[2] *e* Eq S3. *f* Eq S14.

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2 Computational Chemistry

2.1 Optimised geometries

Gaussian[3] input route section:

```
# opt=tight freq=noraman b3lyp/6-31g* scf=tight int=ultrafine
```

Blue dye **1a** (C_{2h})

$E_{SCF} = -2357.69485675$ Ha; rotational $|\tilde{v}| \leq 3.5$ cm^{-1}; vibrational $\tilde{v} \geq 20.8$ cm^{-1} (none imaginary).

C	0.192814	4.371213	0.000000
C	-0.192814	-4.371213	0.000000
C	0.310875	0.622756	0.000000
C	-0.310875	-0.622756	0.000000
C	0.310875	-1.903139	0.000000
C	-0.310875	1.903139	0.000000
C	0.355332	6.710572	0.000000
C	-0.355332	-6.710572	0.000000
C	0.543066	2.977696	0.000000
C	-0.543066	-2.977696	0.000000
C	1.008157	-6.563891	0.000000
C	-1.008157	6.563891	0.000000
C	1.038359	5.468056	0.000000
C	-1.038359	-5.468056	0.000000
C	1.802996	0.738192	0.000000
C	-1.802996	-0.738192	0.000000
H	0.853156	7.673679	0.000000
H	-0.853156	-7.673679	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

H	1.387560	-2.009634	0.000000
H	-1.387560	2.009634	0.000000
H	1.763315	-7.338726	0.000000
H	-1.763315	7.338726	0.000000
H	2.118846	5.375189	0.000000
H	-2.118846	-5.375189	0.000000
O	2.635299	-0.140024	0.000000
O	-2.635299	0.140024	0.000000
S	1.485486	-4.901237	0.000000
S	-1.485486	4.901237	0.000000
S	2.260063	2.508595	0.000000
S	-2.260063	-2.508595	0.000000

Blue dye **1b** (C_{2h}) pentyl groups truncated to methyl groups

$E_{SCF} = -2436.33544484$ Ha; rotational $|\tilde{v}| \leq 2.2$ cm^{-1}; vibrational $\tilde{v} \geq 17.1$ cm^{-1} (none imaginary).

C	0.163234	1.921367	0.000000
C	-0.163234	-1.921367	0.000000
C	0.358030	-0.597529	0.000000
C	-0.358030	0.597529	0.000000
C	0.509785	6.642726	0.000000
C	-0.509785	-6.642726	0.000000
C	0.528869	-4.342585	0.000000
C	-0.528869	4.342585	0.000000
C	0.770475	-2.928503	0.000000
C	-0.770475	2.928503	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

C	0.864592	-6.661724	0.000000
C	-0.864592	6.661724	0.000000
C	1.452665	-5.372590	0.000000
C	-1.452665	5.372590	0.000000
C	1.452665	7.807233	0.000000
C	-1.452665	-7.807233	0.000000
C	1.853735	-0.597363	0.000000
C	-1.853735	0.597363	0.000000
H	0.885711	8.743078	0.000000
H	-0.885711	-8.743078	0.000000
H	1.228463	2.110670	0.000000
H	-1.228463	-2.110670	0.000000
H	1.436517	-7.583863	0.000000
H	-1.436517	7.583863	0.000000
H	2.102384	7.805659	0.883670
H	2.102384	7.805659	-0.883670
H	-2.102384	-7.805659	0.883670
H	-2.102384	-7.805659	-0.883670
H	2.523479	-5.200147	0.000000
H	-2.523479	5.200147	0.000000
O	2.616703	0.342181	0.000000
O	-2.616703	-0.342181	0.000000
S	1.105030	5.002503	0.000000
S	-1.105030	-5.002503	0.000000
S	2.446407	-2.327412	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

S	-2.446407	2.327412	0.000000

Blue dye **1** R = OMe (C_{2h} conformer #1)

$E_{SCF} = -2586.73409656$ Ha; rotational $|\tilde{v}| \leq 1.4$ cm^{-1}; vibrational $\tilde{v} \geq 14.6$ cm^{-1} (none imaginary).

C	0.127265	-1.924302	0.000000
C	-0.127265	1.924302	0.000000
C	0.369162	0.591713	0.000000
C	-0.369162	-0.591713	0.000000
C	0.369162	-6.635116	0.000000
C	-0.369162	6.635116	0.000000
C	0.611235	4.330895	0.000000
C	-0.611235	-4.330895	0.000000
C	0.734822	-8.960149	0.000000
C	-0.734822	8.960149	0.000000
C	0.824459	2.915958	0.000000
C	-0.824459	-2.915958	0.000000
C	1.008160	6.653301	0.000000
C	-1.008160	-6.653301	0.000000
C	1.551878	5.344158	0.000000
C	-1.551878	-5.344158	0.000000
C	1.862436	0.562485	0.000000
C	-1.862436	-0.562485	0.000000
H	0.128482	-9.135690	0.896498
H	0.128482	-9.135690	-0.896498
H	-0.128482	9.135690	0.896498

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

H	-0.128482	9.135690	-0.896498
H	1.189254	-2.131810	0.000000
H	-1.189254	2.131810	0.000000
H	1.598660	-9.625156	0.000000
H	-1.598660	9.625156	0.000000
H	1.605369	7.556048	0.000000
H	-1.605369	-7.556048	0.000000
H	2.618480	5.147052	0.000000
H	-2.618480	-5.147052	0.000000
O	1.264974	-7.633658	0.000000
O	-1.264974	7.633658	0.000000
O	2.609389	-0.390325	0.000000
O	-2.609389	0.390325	0.000000
S	1.023006	-5.013199	0.000000
S	-1.023006	5.013199	0.000000
S	2.488895	2.282245	0.000000
S	-2.488895	-2.282245	0.000000

Blue dye **1** R = OMe (C_{2h} conformer #2)

$E_{SCF} = -2586.73272067$ Ha; rotational $|\tilde{v}| \leq 3.5$ cm^{-1}; vibrational $\tilde{v} \geq 14.7$ cm^{-1} (none imaginary).

C	0.013850	1.927955	0.000000
C	-0.013850	-1.927955	0.000000
C	0.013850	-6.649911	0.000000
C	-0.013850	6.649911	0.000000
C	0.403609	-0.569426	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

C	-0.403609	0.569426	0.000000
C	0.865699	-4.287280	0.000000
C	-0.865699	4.287280	0.000000
C	0.993969	-2.863692	0.000000
C	-0.993969	2.863692	0.000000
C	1.389471	-6.583278	0.000000
C	-1.389471	6.583278	0.000000
C	1.859524	-5.251968	0.000000
C	-1.859524	5.251968	0.000000
C	1.891515	-0.452640	0.000000
C	-1.891515	0.452640	0.000000
C	2.109788	7.723841	0.000000
C	-2.109788	-7.723841	0.000000
H	1.062121	2.196174	0.000000
H	-1.062121	-2.196174	0.000000
H	2.015620	-7.466796	0.000000
H	-2.015620	7.466796	0.000000
H	2.459282	8.756593	0.000000
H	-2.459282	-8.756593	0.000000
H	2.474834	7.209099	0.896938
H	2.474834	7.209099	-0.896938
H	-2.474834	-7.209099	0.896938
H	-2.474834	-7.209099	-0.896938
H	2.913360	-4.995304	0.000000
H	-2.913360	4.995304	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

O	0.683500	7.794750	0.000000
O	-0.683500	-7.794750	0.000000
O	2.582328	0.542248	0.000000
O	-2.582328	-0.542248	0.000000
S	0.728779	5.056513	0.000000
S	-0.728779	-5.056513	0.000000
S	2.618090	-2.133025	0.000000
S	-2.618090	2.133025	0.000000

Blue dye **1c** (C_i) butyl groups truncated to methyl groups

$E_{SCF} = -3232.69758141$ Ha; rotational $|\tilde{v}| \leq 2.2$ cm^{-1}; vibrational $\tilde{v} \geq 10.9$ cm^{-1} (none imaginary).

C	0.033936	0.694217	-0.046219
C	-0.033936	-0.694217	0.046219
C	0.966993	2.868619	-0.017131
C	-0.966993	-2.868619	0.017131
C	1.177391	1.519946	0.136524
C	-1.177391	-1.519946	-0.136524
C	1.181043	-1.504213	0.372131
C	-1.181043	1.504213	-0.372131
C	1.750670	5.280621	-0.082321
C	-1.750670	-5.280621	0.082321
C	1.934890	3.920572	0.109389
C	-1.934890	-3.920572	-0.109389
C	2.930402	6.043892	0.075522
C	-2.930402	-6.043892	-0.075522

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones…*

C	4.034109	5.283940	0.399988
C	-4.034109	-5.283940	-0.399988
C	6.696034	4.997798	-0.419171
C	-6.696034	-4.997798	0.419171
H	0.792227	5.709342	-0.354195
H	-0.792227	-5.709342	0.354195
H	2.145445	1.101515	0.378266
H	-2.145445	-1.101515	-0.378266
H	2.981623	7.118603	-0.055714
H	-2.981623	-7.118603	0.055714
H	6.386012	5.210563	-1.444530
H	-6.386012	-5.210563	1.444530
H	6.678055	3.921726	-0.233343
H	-6.678055	-3.921726	0.233343
H	7.712112	5.369269	-0.261196
H	-7.712112	-5.369269	0.261196
O	2.311782	-1.130002	0.585604
O	-2.311782	1.130002	-0.585604
S	0.720452	-3.273428	0.413587
S	-0.720452	3.273428	-0.413587
S	3.608705	3.589444	0.538809
S	-3.608705	-3.589444	-0.538809
S	5.638164	5.902495	0.780647
S	-5.638164	-5.902495	-0.780647

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

Blue dye **1c** (C_{2h}) butyl groups truncated to methyl groups

$E_{SCF} = -3232.69562542$ Ha; rotational $|\tilde{\nu}| \leq 1.7$ cm^{-1}; vibrational $\tilde{\nu} \geq 12.5$ cm^{-1} (none imaginary).

C	0.059205	-1.926869	0.000000
C	-0.059205	1.926869	0.000000
C	0.059205	-9.421787	0.000000
C	-0.059205	9.421787	0.000000
C	0.149039	-6.654681	0.000000
C	-0.149039	6.654681	0.000000
C	0.390095	0.578114	0.000000
C	-0.390095	-0.578114	0.000000
C	0.763315	4.306066	0.000000
C	-0.763315	-4.306066	0.000000
C	0.927550	2.883819	0.000000
C	-0.927550	-2.883819	0.000000
C	1.230395	6.608817	0.000000
C	-1.230395	-6.608817	0.000000
C	1.737618	5.287985	0.000000
C	-1.737618	-5.287985	0.000000
C	1.882074	0.496407	0.000000
C	-1.882074	-0.496407	0.000000
H	0.564080	9.407530	0.897654
H	0.564080	9.407530	-0.897654
H	-0.564080	-9.407530	0.897654
H	-0.564080	-9.407530	-0.897654
H	0.667984	-10.328961	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

H	-0.667984	10.328961	0.000000
H	1.113205	-2.171803	0.000000
H	-1.113205	2.171803	0.000000
H	1.862261	7.488154	0.000000
H	-1.862261	-7.488154	0.000000
H	2.797967	5.059331	0.000000
H	-2.797967	-5.059331	0.000000
O	2.594053	-0.482521	0.000000
O	-2.594053	0.482521	0.000000
S	0.839544	-5.048040	0.000000
S	-0.839544	5.048040	0.000000
S	1.242024	-8.032758	0.000000
S	-1.242024	8.032758	0.000000
S	2.568390	2.192812	0.000000
S	-2.568390	-2.192812	0.000000

Structure **9** (C_{2h})

$E_{SCF} = -2357.67984897$ Ha; rotational $|\tilde{v}| \leq 3.2$ cm^{-1}; vibrational $\tilde{v} \geq 17.7$ cm^{-1} (none imaginary).

C	0.099784	-4.569361	0.000000
C	-0.099784	4.569361	0.000000
C	0.116683	-7.067094	0.000000
C	-0.116683	7.067094	0.000000
C	0.147745	0.659494	0.000000
C	-0.147745	-0.659494	0.000000
C	0.274879	3.175928	0.000000

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

C	-0.274879	-3.175928	0.000000
C	1.370681	-5.113755	0.000000
C	-1.370681	5.113755	0.000000
C	1.379184	-6.532618	0.000000
C	-1.379184	6.532618	0.000000
C	1.527338	2.642703	0.000000
C	-1.527338	-2.642703	0.000000
C	1.551118	1.191375	0.000000
C	-1.551118	-1.191375	0.000000
H	0.166065	8.111490	0.000000
H	-0.166065	-8.111490	0.000000
H	2.270863	-4.508750	0.000000
H	-2.270863	4.508750	0.000000
H	2.282779	-7.131532	0.000000
H	-2.282779	7.131532	0.000000
H	2.445629	3.218212	0.000000
H	-2.445629	-3.218212	0.000000
O	2.531327	0.448188	0.000000
O	-2.531327	-0.448188	0.000000
S	1.045361	-1.952868	0.000000
S	-1.045361	1.952868	0.000000
S	1.107111	5.846142	0.000000
S	-1.107111	-5.846142	0.000000

Di-*tert*-butoxy **16** (*C*$_1$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

$E_{SCF} = -1569.74533396$ Ha; rotational $|\tilde{\nu}| \leq 3.7$ cm^{-1}; vibrational $\tilde{\nu} \geq 17.9$ cm^{-1} (none imaginary).

C	0.320665	-0.520929	-0.598487
C	-0.490927	0.708575	-0.549836
C	1.582194	-0.663649	-0.052285
C	-1.872153	0.719492	-0.507674
C	0.036020	2.047486	-0.574995
C	-0.120797	-1.741468	-1.225021
C	0.766689	-2.768403	-1.139024
C	-2.433835	-0.823367	1.861272
C	-0.912004	3.024622	-0.568791
C	-3.384828	-0.835277	0.663701
C	3.599712	0.677371	0.483882
C	3.869346	0.896044	-1.007306
C	3.686349	1.992579	1.262918
C	-3.780303	-2.262788	0.282766
C	4.559383	-0.356646	1.087678
C	-4.626453	0.026002	0.916954
H	1.096597	2.256483	-0.603379
H	-1.537959	-1.415976	1.654059
H	-1.071971	-1.815327	-1.735862
H	-2.122523	0.194139	2.116423
H	3.188407	1.643116	-1.427487
H	-2.889482	-2.869461	0.093268
H	3.756513	-0.030617	-1.577347
H	0.690749	-3.758765	-1.567084

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones…*

H	2.986715	2.731149	0.859964
H	-2.939545	-1.251824	2.733716
H	-0.766005	4.096262	-0.584208
H	3.438092	1.827203	2.316044
H	-4.355779	1.053178	1.179776
H	4.569839	-1.291246	0.519623
H	4.275838	-0.578515	2.121373
H	-4.396879	-2.258767	-0.622037
H	4.895029	1.255137	-1.145316
H	-4.354454	-2.728070	1.091109
H	-5.263469	0.049674	0.026637
H	4.699436	2.404077	1.204192
H	-5.209783	-0.388689	1.747090
H	5.581121	0.039763	1.087977
O	2.207025	0.255798	0.716281
O	-2.701683	-0.347467	-0.556529
S	2.198964	-2.311073	-0.262983
S	-2.518187	2.364358	-0.535833

Diboronic ester **18** (C_1)

$E_{SCF} = -2391.14424302$ Ha; rotational $|\tilde{v}| \leq 2.9$ cm^{-1}; vibrational $\tilde{v} \geq 6.7$ cm^{-1} (none imaginary).

B	4.454310	0.328367	0.364596
B	-4.459828	-0.411316	0.443887
C	0.630169	0.255657	-0.143686
C	-0.635721	-0.489265	-0.023227

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones…*

C	0.748200	1.544440	-0.648240
C	-1.923286	0.105130	0.153366
C	1.909024	-0.259207	0.239649
C	-0.738815	-1.873356	-0.051023
C	2.975772	0.581626	0.033937
C	-2.976374	-0.770270	0.267502
C	0.499116	-2.574300	-2.573685
C	-0.564422	3.646058	-0.853374
C	0.576685	-3.502572	-1.360607
C	-0.490287	3.860362	0.660747
C	-1.996278	3.821440	-1.368178
C	2.005131	-3.997579	-1.127373
C	0.387562	4.580965	-1.610178
C	-0.394887	-4.680686	-1.484688
C	-6.349826	0.866983	0.481596
C	6.303784	-0.694149	1.222080
C	6.718396	0.605007	0.425493
C	-6.690115	-0.624344	0.875084
C	6.274609	-0.492567	2.743413
C	-6.704245	1.209557	-0.972045
C	-6.851474	-0.834587	2.386886
C	-6.908992	1.931852	1.423319
C	7.258533	0.311541	-0.980864
C	7.097654	-1.951996	0.874349
C	7.664641	1.548784	1.165224

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

C	-7.872373	-1.241045	0.129921
H	-2.071676	1.174864	0.194258
H	2.028346	-1.239154	0.683688
H	1.179972	-1.725759	-2.459007
H	-0.514480	-2.187289	-2.717203
H	-1.173100	3.185845	1.187090
H	0.521435	3.695947	1.042526
H	-2.690079	3.156653	-0.844304
H	2.694633	-3.155005	-1.017855
H	0.781501	-3.126729	-3.476776
H	-2.044586	3.593571	-2.437778
H	-1.422259	-4.340559	-1.645182
H	1.412352	4.519537	-1.233465
H	-0.777913	4.890300	0.898637
H	2.053763	-4.603671	-0.216871
H	0.391887	4.335445	-2.676937
H	-0.368080	-5.295215	-0.578854
H	-2.326643	4.854792	-1.217990
H	2.335565	-4.613141	-1.971015
H	-0.113518	-5.310341	-2.336642
H	0.055433	5.619236	-1.496862
H	5.704986	0.401577	3.015586
H	-6.306836	0.461786	-1.665483
H	-6.010397	-0.405640	2.940612
H	-6.258202	2.175977	-1.226934

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

H	5.786669	-1.356275	3.205527
H	6.591582	-0.359591	-1.531146
H	-6.551773	1.793971	2.446265
H	-6.590573	2.923529	1.085842
H	7.016053	-2.200862	-0.186103
H	6.711780	-2.799461	1.450019
H	7.325354	1.251304	-1.537684
H	-6.877798	-1.908864	2.593742
H	7.237190	1.889774	2.110759
H	-7.715809	-1.235775	-0.951063
H	7.283532	-0.402480	3.159877
H	-7.787089	1.280507	-1.119800
H	7.860117	2.430566	0.546555
H	-7.778831	-0.388283	2.761435
H	8.255510	-0.140403	-0.945986
H	-8.002118	-2.281015	0.446181
H	-8.004918	1.912433	1.429170
H	8.157567	-1.827245	1.124488
H	8.623831	1.059431	1.370230
H	-8.799844	-0.700956	0.352682
O	-0.264444	2.244108	-1.200912
O	0.281630	-2.756684	-0.115543
O	-4.897577	0.889200	0.574495
O	4.925263	-0.890556	0.798995
O	5.441339	1.280428	0.249897

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

O	-5.480695	-1.331792	0.482024
S	2.424144	2.082122	-0.685023
S	-2.396154	-2.417564	0.171232

2.2   Time-dependent density functional theory

Gaussian[3] input route sections:

```
# td=(nstates=5,root=1) lsda/6-311++g** scf=tight

# td=(nstates=5,root=1) blyp/6-311++g** scf=tight

# td=(nstates=5,root=1) b3lyp/6-311++g** scf=tight

# td=(nstates=5,root=1) bhandhlyp/6-311++g** scf=tight
```

Table S2. TDDFT Data for Transitions from the Ground State to the First Singlet Excited State.[a]

		LSDA		BLYP		**B3LYP**		BHandHLYP	
Dye	Point group	$\tilde{\nu}_{0-0}$ /cm^{-1}	f	$\tilde{\nu}_{0-0}$ /cm^{-1}	f	$\tilde{\nu}_{0-0}$ /cm^{-1}	f	$\tilde{\nu}_{0-0}$ /cm^{-1}	f
9	C_{2h}	16,977	0.1350	17,155	0.1165	**19,992**	**0.1863**	24,352	0.2377
1a	C_{2h}	14,280	0.5107	14,361	0.5280	**15,788**	**0.6672**	17,803	0.8767
1b[b]	C_{2h}	14,085	0.6120	14,224	0.6470	**15,509**	**0.7662**	17,430	0.9757
1 R = OMe	C_{2h} (#1)	13,950	0.7490	14,092	0.7867	15,297	0.8864	17,170	1.0846
	C_{2h} (#2)	13,788	0.7212	13,915	0.7523	15,069	0.8516	16,856	1.0435
1c[b]	C_i	13,003	0.7655	13,281	0.7963	**14,916**	**0.9012**	16,997	1.0767
	C_{2h}	13,303	0.9655	13,442	0.9770	14,687	1.0438	16,651	1.2182

a Data in boldface appear in Table 1 of the main article. *b* The alkyl chains of **1b** and **1c** were truncated to methyl groups.

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

Table S3. TDDFT Data for Transitions from the Ground State to the Second (Allowed) Singlet Excited State.

Dye	Point group	LSDA $\tilde{v}_{0-0}$ /cm^{-1}	f	BLYP $\tilde{v}_{0-0}$ /cm^{-1}	f	B3LYP $\tilde{v}_{0-0}$ /cm^{-1}	f	BHandHLYP $\tilde{v}_{0-0}$ /cm^{-1}	f
9	C_{2h}	19,751	0.5035	19,764	0.4777	24,062	0.6870	29,323	1.1719
1a	C_{2h}	20,532	0.2728	20,686	0.2193	24,911	0.2962	31,469	0.5249
1b[a]	C_{2h}	19,778	0.2587	20,028	0.2140	24,224	0.2843	30,759	0.5328
1 R = OMe	C_{2h} (#1)	18,803	0.1860	19,159	0.1530	23,411	0.2381	30,088	0.4963
	C_{2h} (#2)	19,186	0.1526	19,467	0.1190	23,670	0.2069	30,214	0.4951
1c[a]	C_i	15,506	0.0262	16,117	0.0260	21,066	0.1317	28,657	0.4266
	C_{2h}	17,170	0.0949	17,584	0.0850	21,675	0.2013	28,362	0.4702

a The alkyl chains of **1b** and **1c** were truncated to methyl groups.

3   X-ray Crystallography

The structures of both **1b** and **1c** were found to have a centre of symmetry in the middle of the C(3)=C(3A) bond.

Though a strong scatterer, the crystal of **1b** that was studied was clearly multiply twinned, giving very smeared and streaky diffraction peaks. However, thanks to the small triclinic unit cell [volume of 590.9(3) Å^3] and the use of Cu-Kα radiation, the peaks were well separated from each other allowing for reasonable estimates of the correct intensities. As such, the final structural model is much better than might have been expected given the peak shapes.

The peak shapes in the diffraction patterns of the crystal of **1c**, by contrast, are very good, so it is no surprise that the final structure is also very good.

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
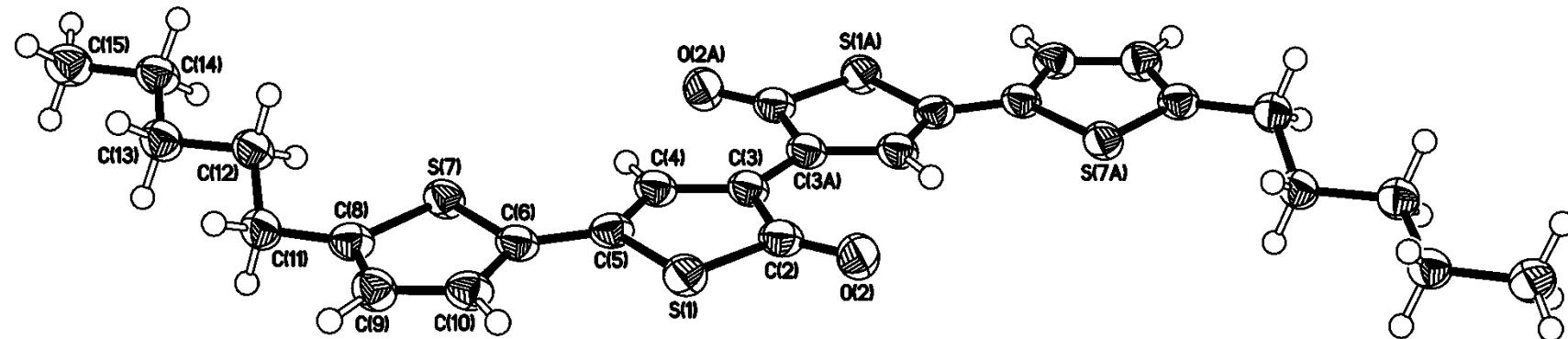
Figure S2. The crystal structure of **1b** (50% probability ellipsoids). Atoms labelled with an "A" after the number are related to their counterparts

without the letter by the centre of symmetry situated in the middle of the C(3)=C(3A) bond.
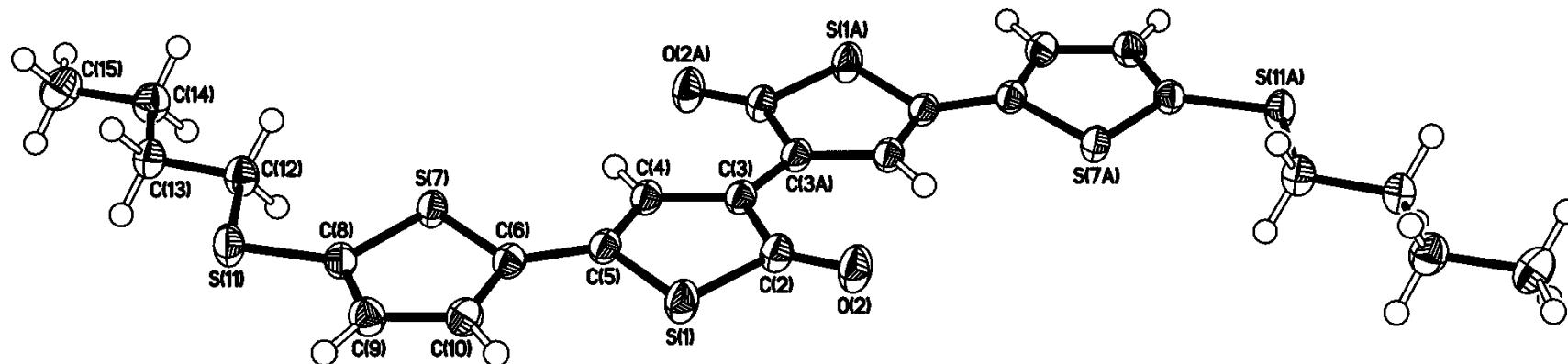
Figure S3. The crystal structure of **1c** (50% probability ellipsoids). Atoms labelled with an "A" after the number are related to their counterparts

without the letter by the centre of symmetry situated in the middle of the C(3)=C(3A) bond.

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
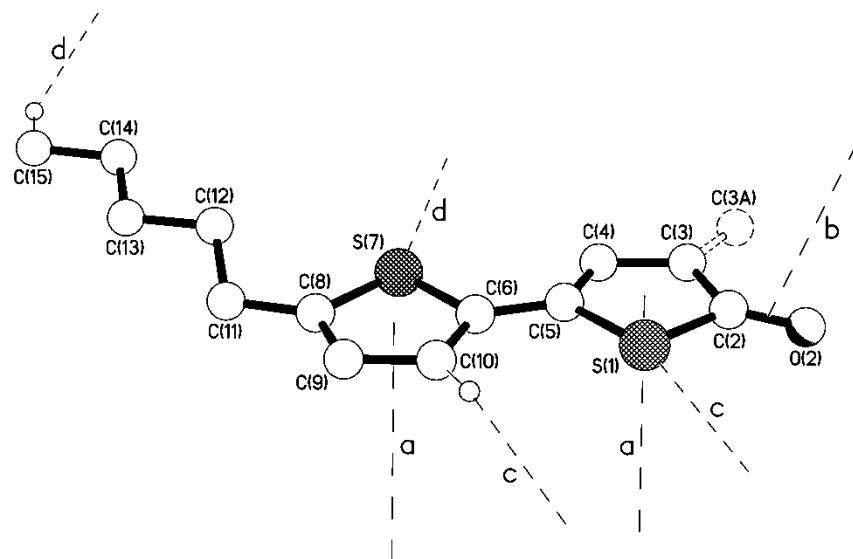
Figure S4. The unique portion of the crystal structure of **1b** showing the intermolecular π-π and C–H···S interactions. The π-π interaction **a** has centroid···centroid and mean interplanar separations of *ca.* 3.77 Å and 3.45 Å respectively, the two rings being inclined by *ca.* 3°. Interaction **b**, which links two carbonyl groups across a centre of symmetry has a centroid···centroid separation of *ca.* 3.24 Å. The C–H···S contacts **c** and **d** have H···S separations of *ca.* 2.84 Å and 2.97 Å respectively.
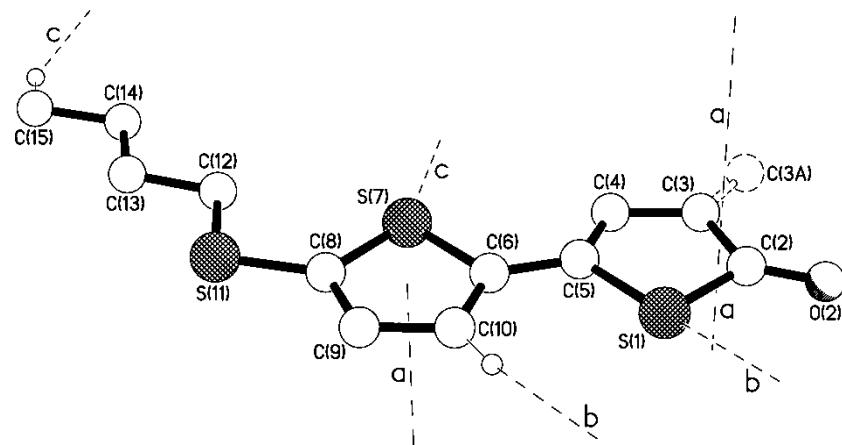
Figure S5. The unique portion of the crystal structure of **1c** showing the intermolecular π-π and C–H···S interactions. For π-π interaction **a** the centroid···centroid and mean interplanar separations are both *ca.* 3.36 Å, the two planes being inclined by *ca.* 3°. The C–H···S contacts **b** and **c** have H···S separations of *ca.* 2.88 Å and 3.10 Å respectively.

Figure S6. Part of one of the sheets of C–H⋯S linked molecules present in the crystal of **1b**.

Interactions **c** and **d** have H⋯S separations of *ca.* 2.84 Å and 2.97 Å respectively.
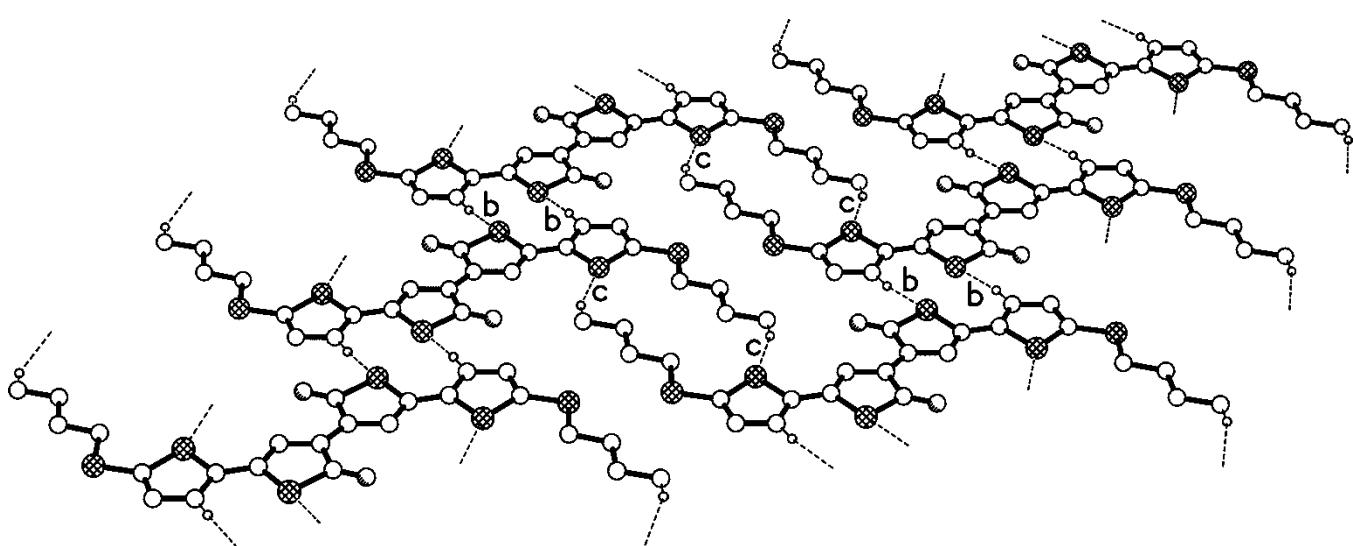
Figure S7. Part of one of the sheets of C–H⋯S linked molecules present in the crystal of **1c**.

Interactions **b** and **c** have H⋯S separations of *ca.* 2.88 Å and 3.10 Å respectively.

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
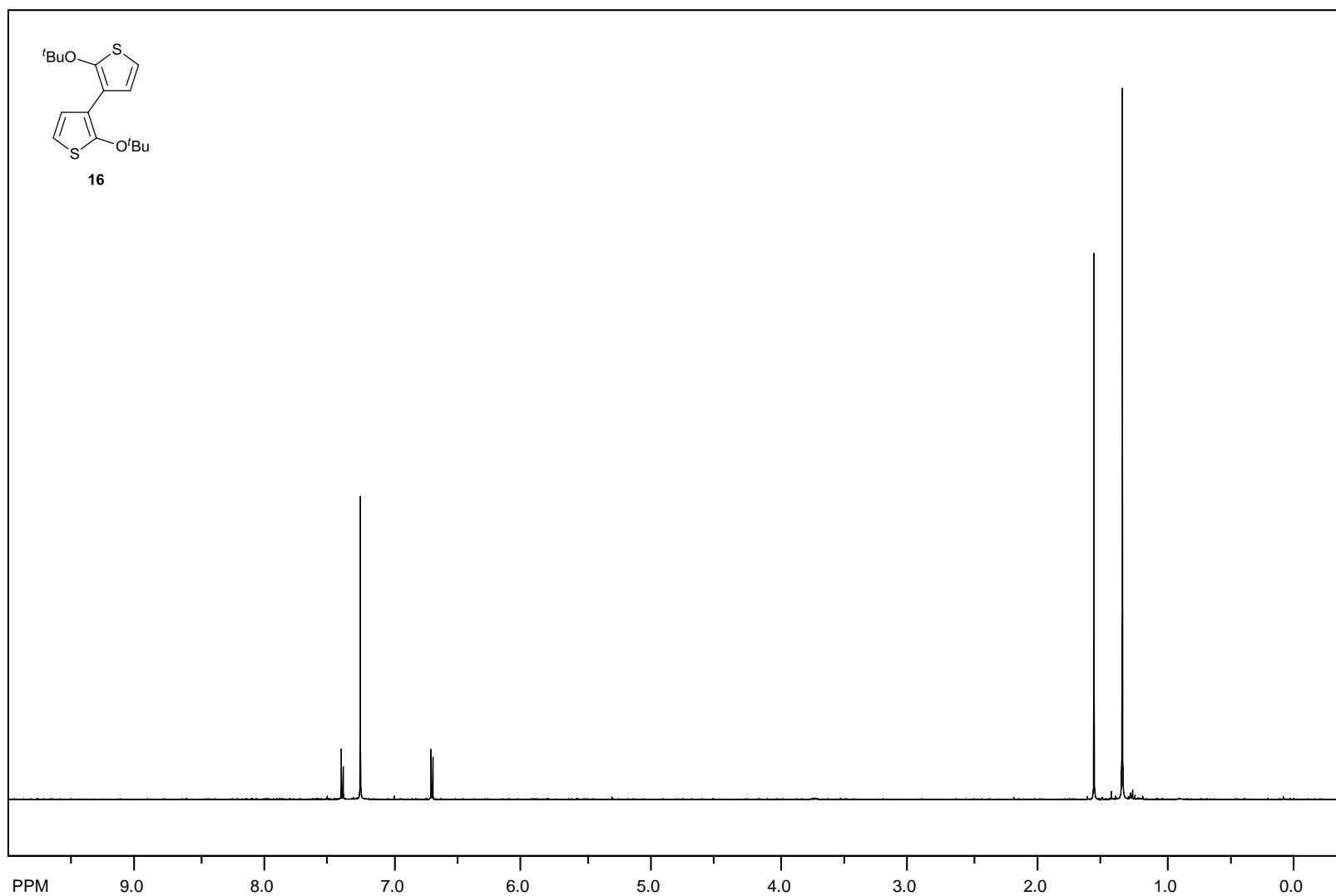
^{1}H NMR (400 MHz; CDCl$_3$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
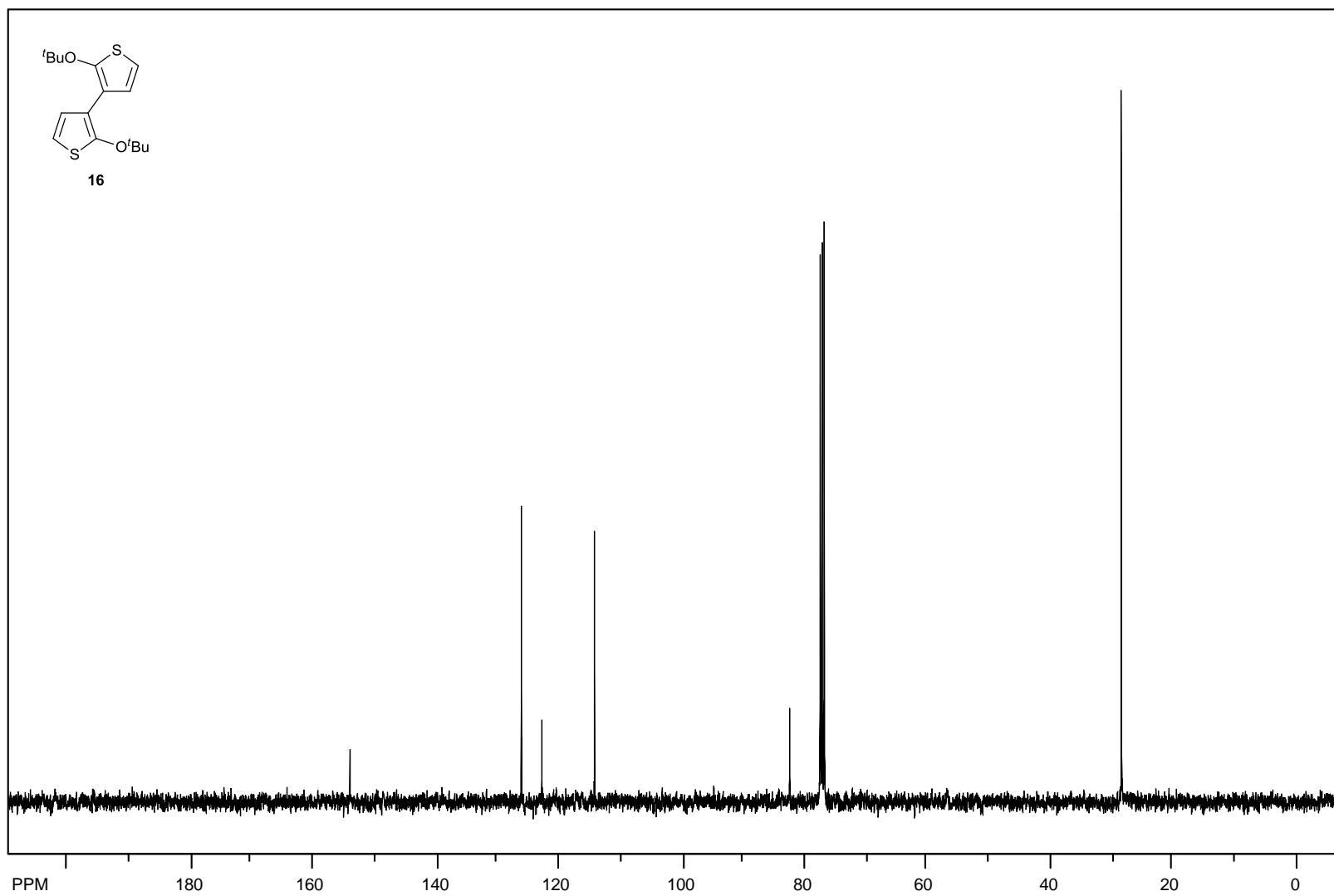
^{13}C NMR (100 MHz; CDCl$_3$)

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…*
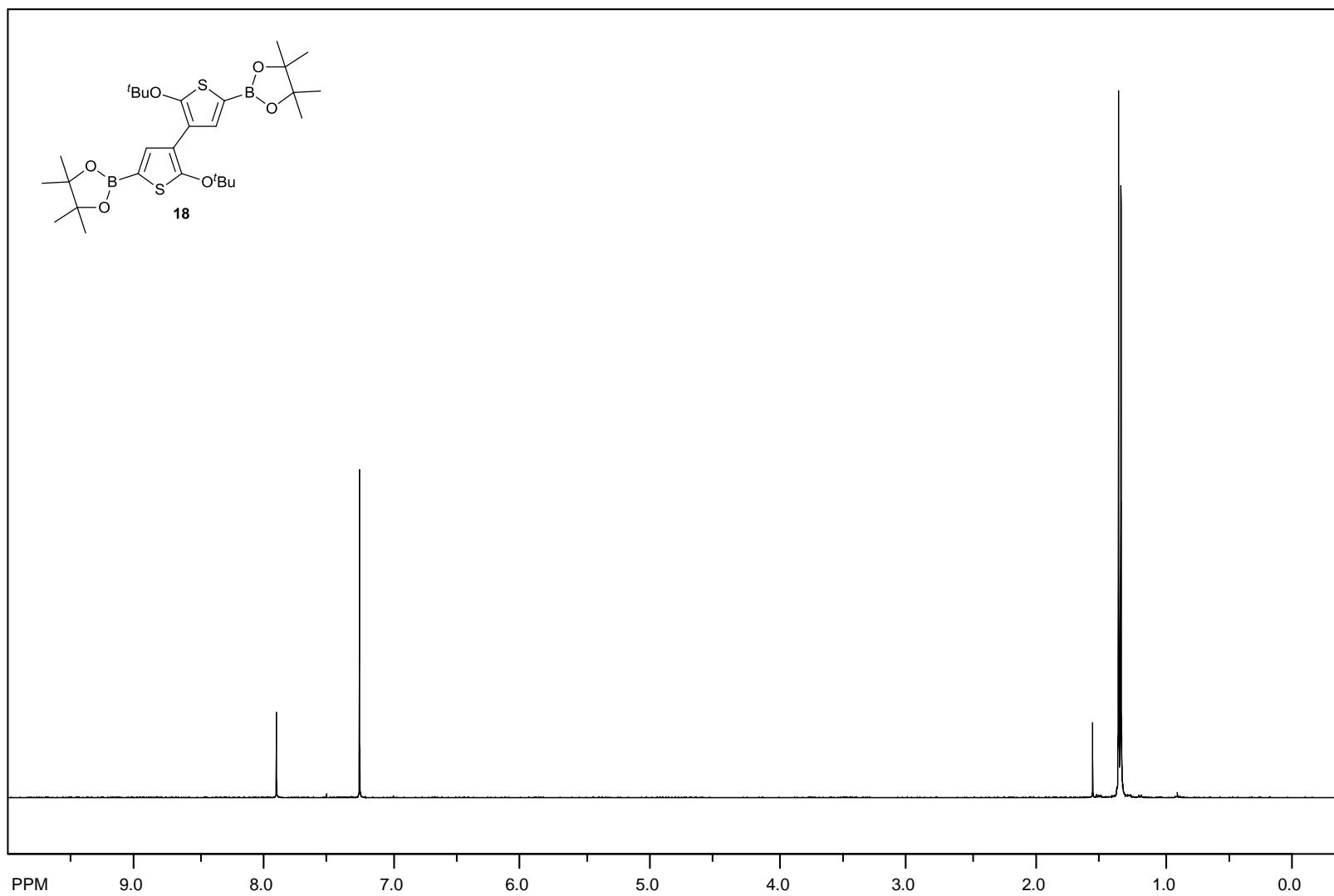
^{1}H NMR (400 MHz; CDCl$_3$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
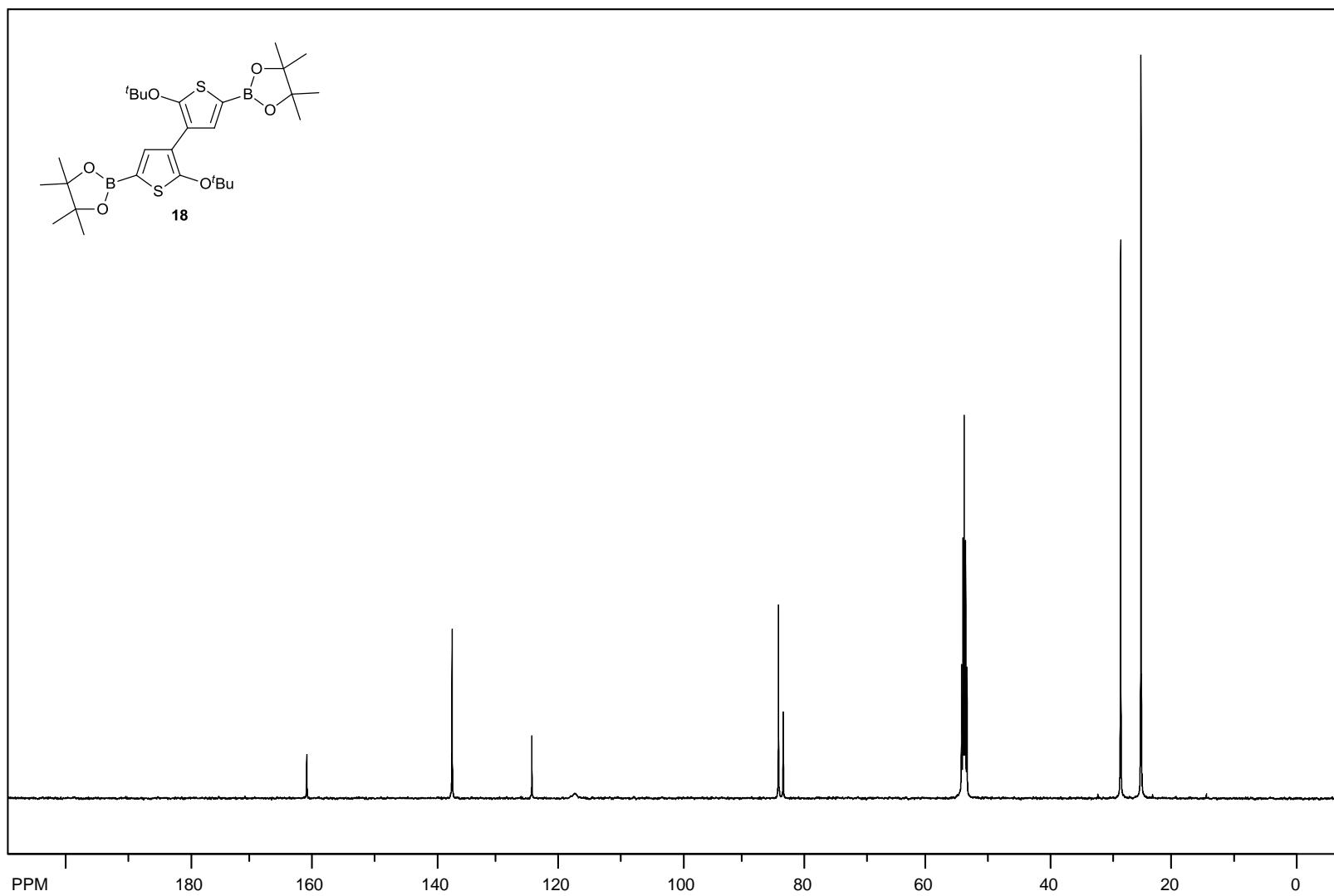
^{13}C NMR (125 MHz; CD$_2$Cl$_2$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
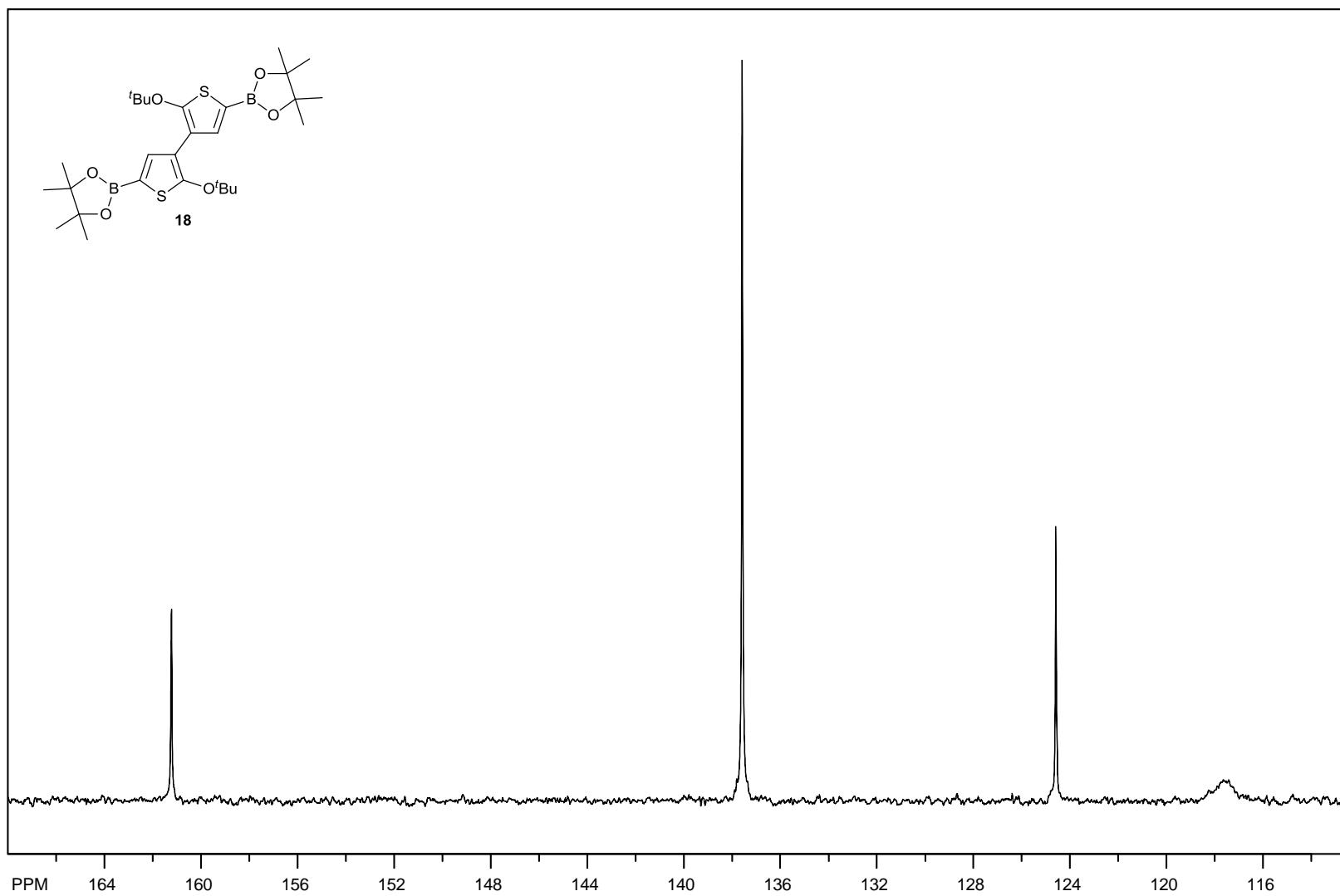
^{13}C NMR (125 MHz; CD$_2$Cl$_2$) expansion

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
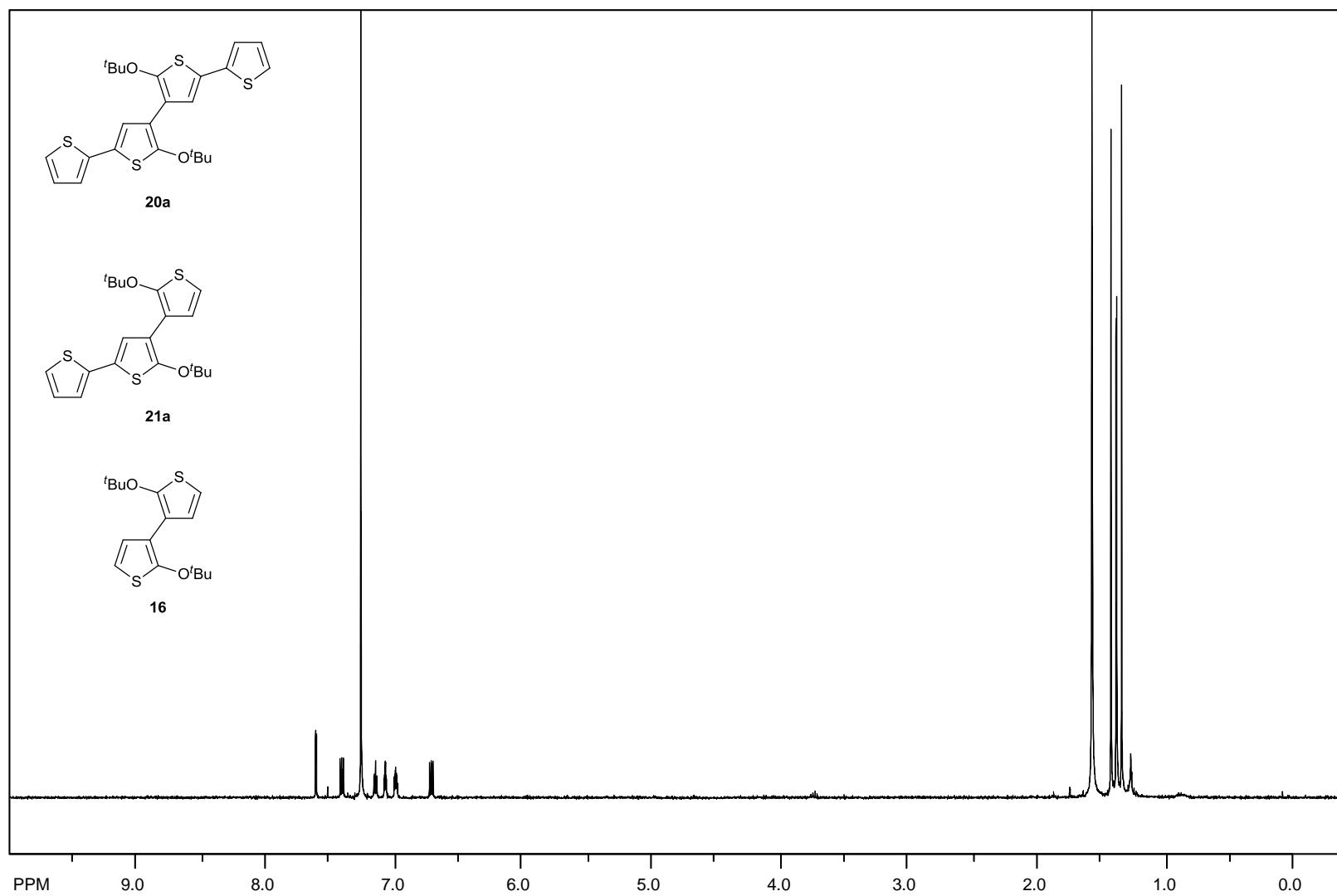
^{1}H NMR (400 MHz; CDCl$_3$)

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…*

Inseparable mixture
20a, **21a** and **16**

^{1}H NMR (400 MHz; CDCl$_3$) expansion

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones…*

1a
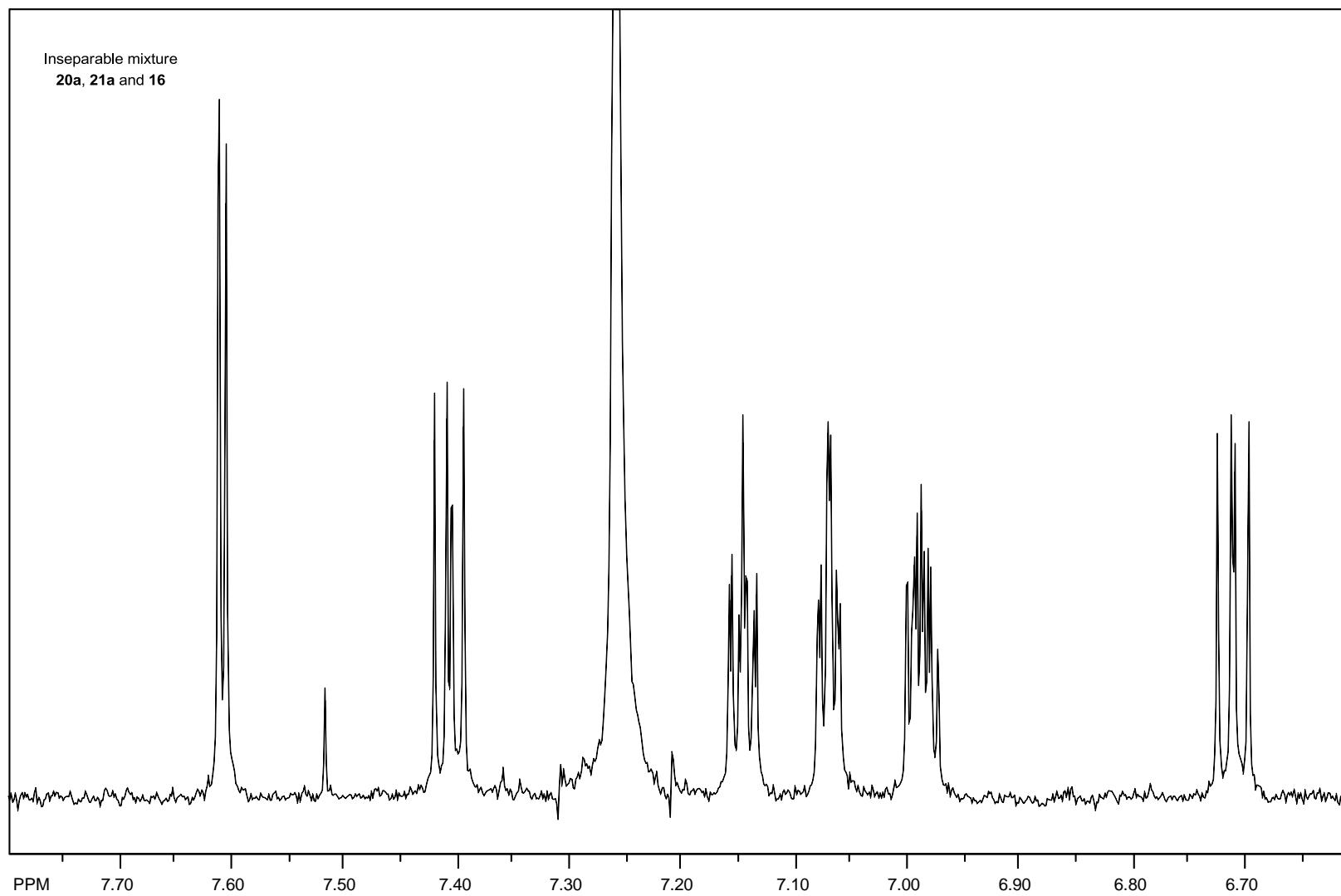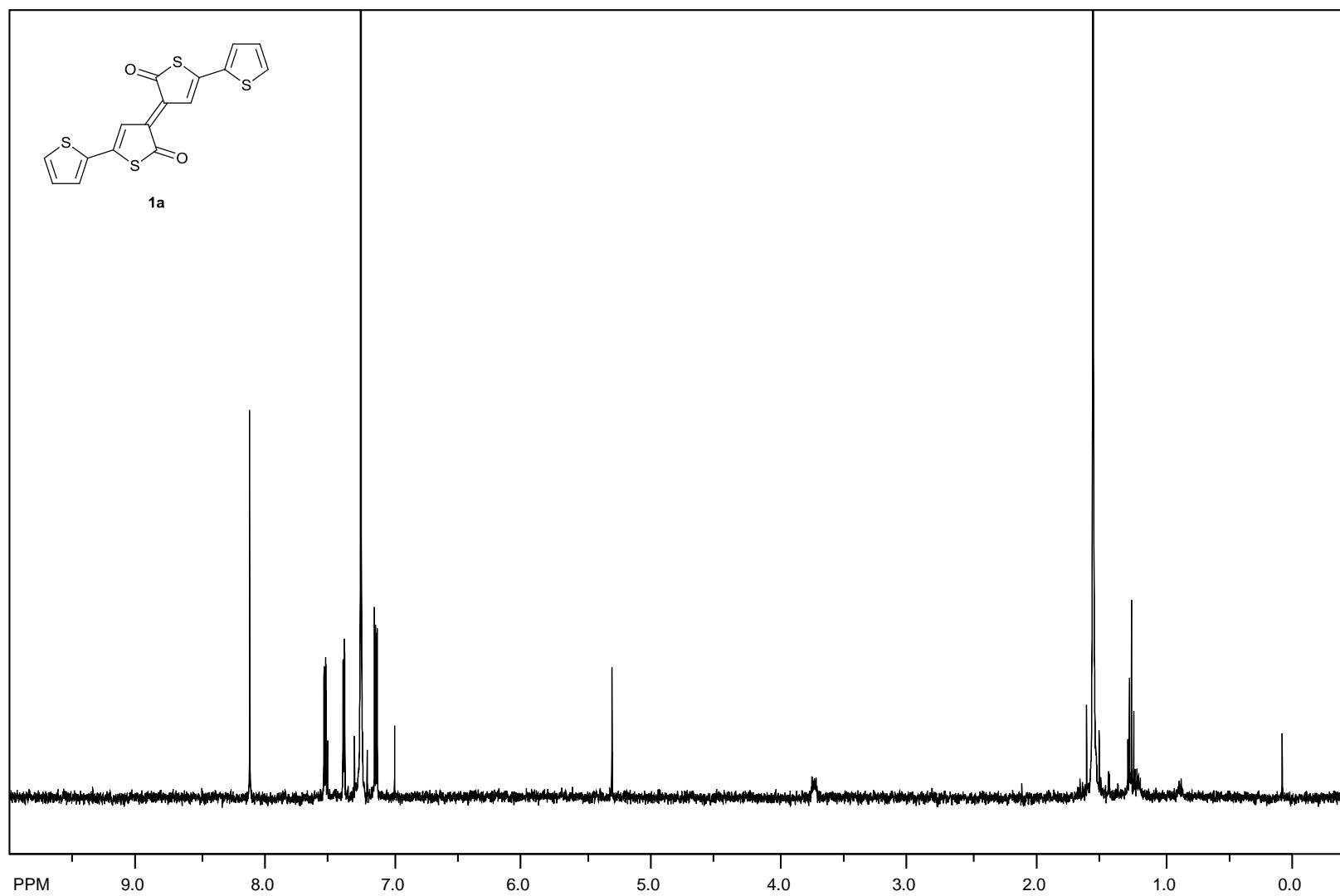
^{1}H NMR (400 MHz; CDCl$_3$) Weak signals because of poor solubility of **1a**. (Not sufficiently soluble for ^{13}C NMR analysis.)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…
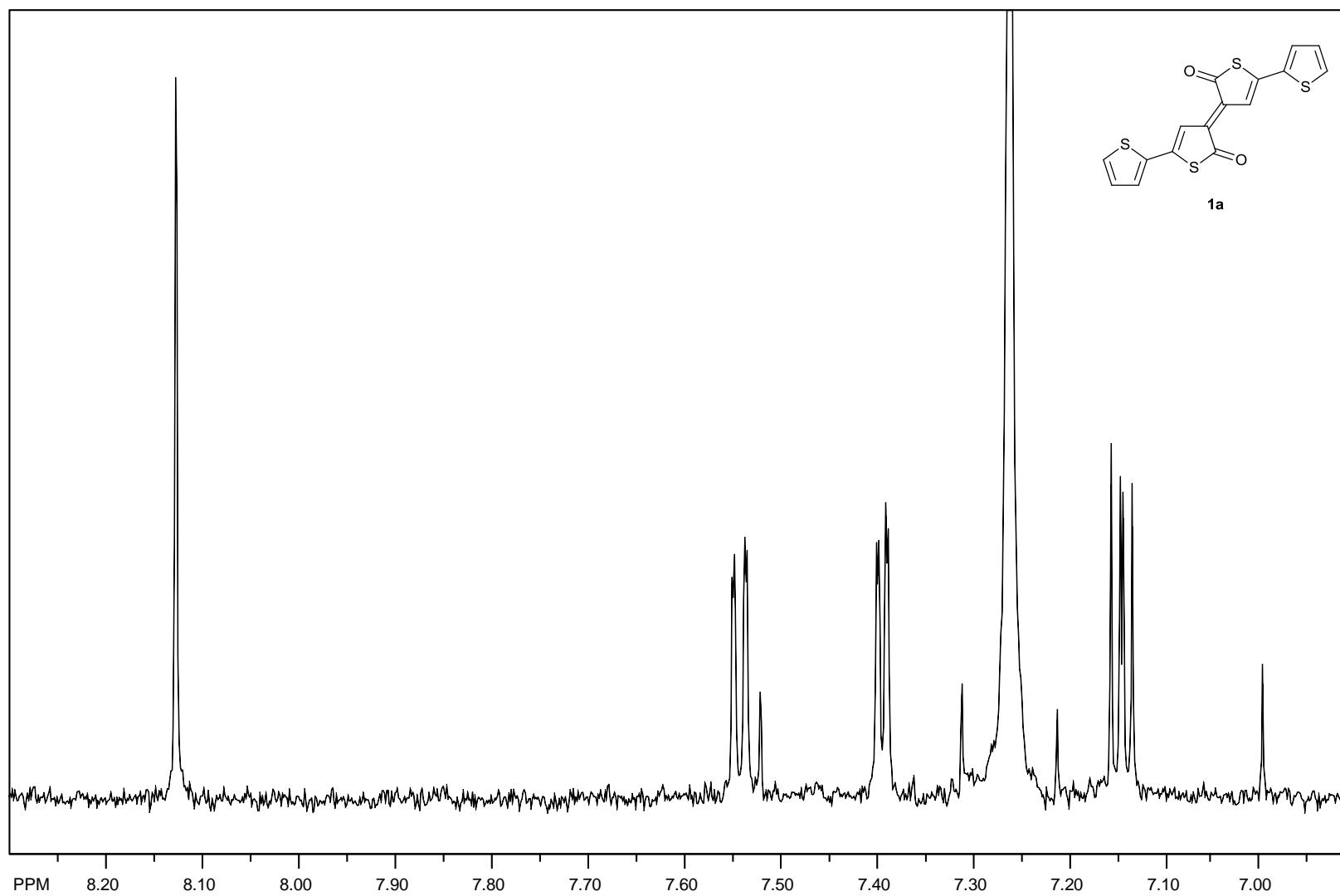
^{1}H NMR (400 MHz; CDCl$_3$) expansion. Weak signals because of poor solubility of **1a**.

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2*H*)-ylidene]-2,2'-diones…*

^{1}H NMR (400 MHz; CDCl$_3$)

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…*

Inseparable mixture
20b, **21b** and **16**

^{1}H NMR (400 MHz; CDCl$_3$) expansion

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

^{1}H NMR (400 MHz; CDCl$_3$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

^{13}C NMR (100 MHz; CDCl$_3$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones...

Inseparable mixture

^{1}H NMR (400 MHz; CDCl$_3$)

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

Inseparable mixture
20c, **21c** and **16**

^{1}H NMR (400 MHz; CDCl$_3$) expansion

(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…

^{1}H NMR (400 MHz; CDCl$_3$)

*(E)-5,5'-Di(thiophen-2-yl)-3,3'-bi[thiophen-3(2H)-ylidene]-2,2'-diones…*

^{13}C NMR (100 MHz; CDCl$_3$)
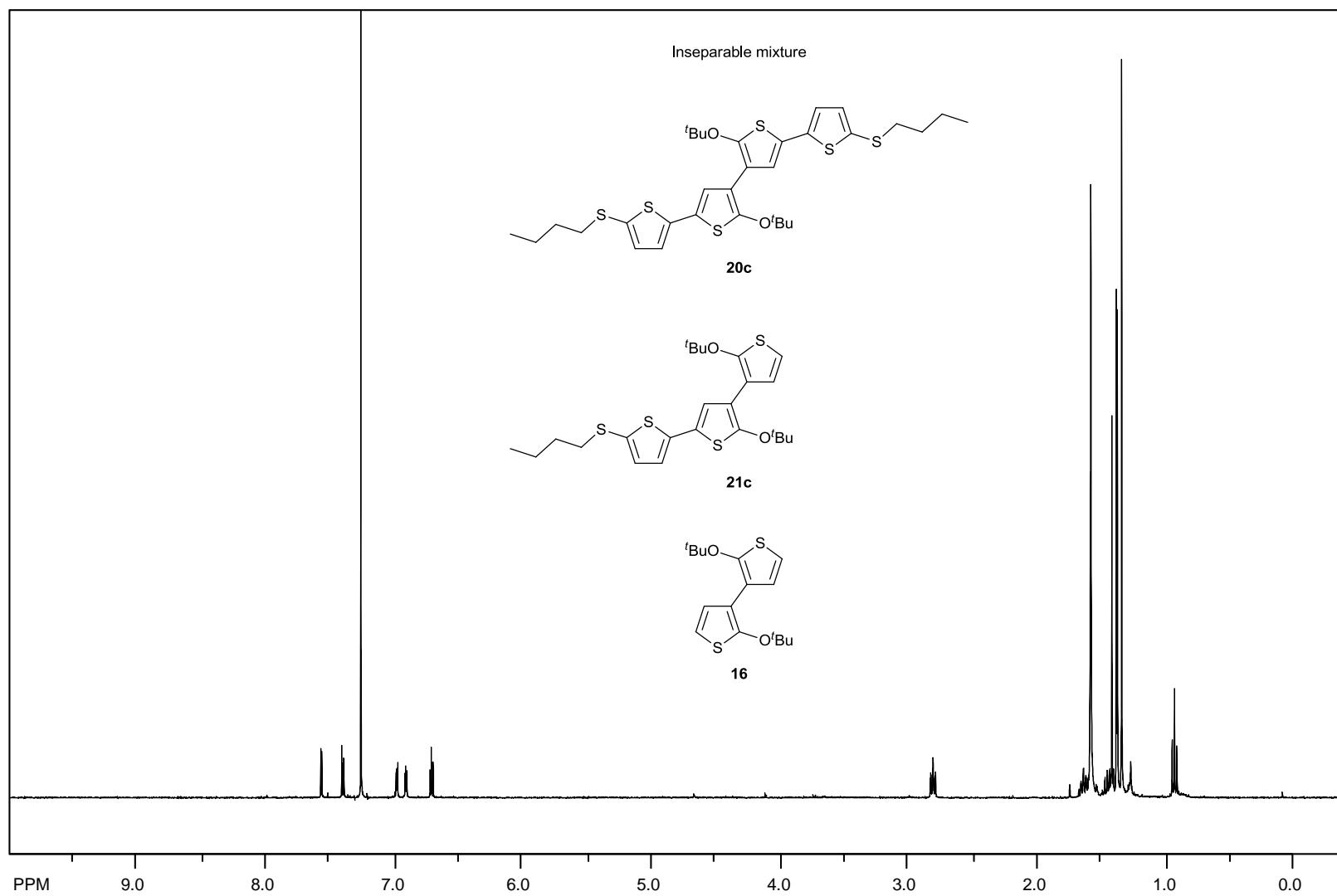
5   References (Supplementary Information)

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