Supporting Information for

Tricolor mechanochromic luminescence of an organic two-component dye:
visualization of a crystalline state and two amorphous states

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Table of contents

1. The mechanochromic luminescence of 1 .......................................................... S2
2. The mechanochromic luminescence of the two-component dye 1/DMQA .................. S3
3. DSC analyses of 1 and the two-component dye 1/DMQA ................................... S7
4. Measurement of the fluorescence lifetimes ......................................................... S8
5. References ........................................................................................................... S9
6. NMR spectra of 1 ............................................................................................... S10
1. The mechanochromic luminescence of I

The emission maximum of crystalline bithiophene I (B-C; $\lambda_{em}$ = 488 nm) was by 13 nm bathochromically shifted upon grinding with a spatula (B-G; $\lambda_{em}$ = 501 nm). B-C liquefied upon heating to 150 °C and the fluorescence spectrum of the molten sample (B-M; $\lambda_{em}$ = 500 nm) was recorded after cooling the sample rapidly to room temperature. The fluorescence spectrum of B-M was in good agreement with that of B-G (Figure S1).

![Normalized fluorescence spectra of the mechanochromic luminescence of I](image)

**Figure S1** Normalized fluorescence spectra of the mechanochromic luminescence of I (B-C = blue solid line; B-M = green solid line; B-G = green dotted line).

The PXRD analysis of B-C, prepared by heating B-G to 100 °C followed by cooling to room temperature, confirmed the crystallinity of B-C (Figure S2a). Conversely, diffraction peaks were not observed for B-M and B-G, indicating that both samples are amorphous (Figure S2b,c).

![PXRD patterns for B-C (a), B-M (b), and B-G (c)](image)

**Figure S2** PXRD patterns for B-C (a), B-M (b), and B-G (c).
2. The mechanochromic luminescence of the two-component dye 1/DMQA

The solid-state absorption spectrum of DMQA overlaps well with the solid-state emission spectrum of B-G (Figure S3), which should lead to an efficient energy transfer from B-G to DMQA.

![Figure S3](image)

**Figure S3** Solid-state absorption spectra of B-C and DMQA, as well as the emission spectrum of B-G.

The maximum emission wavelengths of BD-M, BD-G, and BD-C were observed within experimental errors during six heating–grinding cycles between BD-M and BD-G (Figure S4a) as well as between BD-G and BD-C (Figure S4b), supporting the absence of thermal decomposition for 1 and DMQA.

![Figure S4](image)

**Figure S4** Plots of the emission maxima during six heating–grinding cycles: (a) BD-M and BD-G (b) BD-C and BD-G.
In toluene, emission maxima of DMQA were observed at 525 nm (stronger) and 559 nm (weaker), which are in the same region as those of BD-M. In polar DMSO, the solvatofluorochromatic nature of DMQA is reflected in bathochromically shifted emission maxima at 546 nm (stronger) and 578 nm (weaker) (Figure S5).

**Figure S5** Normalized fluorescence spectra of DMQA in toluene and DMSO.
The fluorescence spectra of BD-M remained almost unchanged upon changing the molar ratio of 1 and DMQA from 1:1 to 4:1. In contrast, a hypsochromic shift of the emission maximum was observed for BD-G upon increasing the molar ratio of 1 (Figure S6).

Figure S6 Fluorescence spectra of BD-M and BD-G prepared from I/DMQA with different mixing ratios: (a) I/DMQA = 1:1; (b) I/DMQA = 2:1; (c) I/DMQA = 3:1; (d) I/DMQA = 4:1.
Figure S7 Solid-state absorption spectra of BD-C, BD-M, and BD-G.

In the solid-state $^{13}$C NMR spectra, considerable shifts of the signals were observed between crystalline BD-C and amorphous BD-M and BD-G. Significant differences of the chemical shift values for the hexyl groups were observed between amorphous BD-M ($\delta = 31.38, 23.13, 14.66$ ppm) and BD-G ($\delta = 31.93, 23.58, 14.98$ ppm) (Figure S8).

Figure S8 Solid-state $^{13}$C NMR spectra of BD (a), BD-M (b), and BD-G (c).

* Denotes spinning sidebands.
3. DSC analyses of 1 and the two-component dye 1/DMQA

Similar thermal behavior was observed in the DSC thermograms of B-C, B-D, B-M, and BD-M, as well as B-G and BD-G. Therefore, the fraction of bithiophene 1 in the two-component dye BD-C, BD-M, and BD-G should be in the same state as in B-C, B-M, and B-G, respectively (Figure S9).

Figure S9 DSC thermograms for B-C (a), B-M (b), B-G (c), BD-C (d), BD-M (e), and BD-G (f). $T_m$, $T_c$, and $T_g$ values are noted near the corresponding peaks and steps.
4. Measurement of the fluorescence lifetimes

Fluorescence lifetime decays were measured upon excitation at 410 nm and detection of the emission at 470 nm (BD-C), 531 nm (BD-M), 592 nm (BD-G), and 648 nm (DMQA). The decay curves display complex multi-exponential behavior that required three components to fit the experimental data (Figure S10 and Table S1).

![Figure S10](image)

**Figure S10** Fluorescence lifetime decay of BD-C (a), BD-M (b), BD-G (c), and DMQA (d) in the solid state at room temperature.

**Table S1.** Fluorescence lifetime ($\tau_n$) and area-weighted mean fluorescence lifetime ($\ll<\tau_F>\gg$) of BD-C, BD-M, BD-G, and DMQA in the solid state at room temperature.

<table>
<thead>
<tr>
<th>State</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\ll&lt;\tau_F&gt;\gg$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BD-C</td>
<td>0.5 (5.8%)</td>
<td>2.9 (31.9%)</td>
<td>6.7 (62.3%)</td>
<td>5.1</td>
</tr>
<tr>
<td>BD-M</td>
<td>0.6 (6.7%)</td>
<td>4.5 (18.8%)</td>
<td>13.0 (74.5%)</td>
<td>10.6</td>
</tr>
<tr>
<td>BD-G</td>
<td>0.7 (5.0%)</td>
<td>4.1 (28.2%)</td>
<td>13.9 (66.9%)</td>
<td>10.5</td>
</tr>
<tr>
<td>DMQA</td>
<td>0.5 (20.4%)</td>
<td>1.8 (43.4%)</td>
<td>5.6 (36.2%)</td>
<td>3.0</td>
</tr>
</tbody>
</table>

*a* Excitation wavelength for the measurement of the fluorescence lifetime: 410 nm. *b* The area-weighted ratio $[(A_n*\tau_n)/\Sigma(A_n*\tau_n)]$ is shown in parentheses, where $A_n$ refers to the coefficient of the $n$-th component.

c Area-weighted mean fluorescence lifetime. $\ll<\tau_F>\gg = \Sigma(A_n*\tau_n^2)/\Sigma(A_n*\tau_n)$. 

S8
5. References

$^1$H NMR spectrum of 1 (500 MHz, in CDCl$_3$, 283 K)
Partial $^1$H NMR spectrum of 1 (500 MHz, in CDCl$_3$, 283 K)
$^{13}$C NMR spectrum of 1 (126 MHz, in CDCl$_3$, 283K)
Partial $^{13}$C NMR spectrum of 1 (126 MHz, in CDCl$_3$, 283 K)
Partial COSY spectrum of 1 (500 MHz, in CDCl$_3$, 283 K)
Partial HSQC spectrum of 1 (500 MHz, in CDCl₃, 283 K)
Partial HSQC spectrum of 1 (500 MHz, in CDCl₃, 283 K)
Partial HMBC spectrum of 1 (500 MHz, in CDCl$_3$, 283 K)
Partial HMBC spectrum of 1 (500 MHz, in CDCl$_3$, 283 K)
Partial HMBC spectrum of 1 (500 MHz, in CDCl₃, 283 K)