Supporting Information for
Lifetime-Ultra-Prolonged Luminescent Multilayer Thin Films with Electronic Microenvironment
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Supplementary Information

List of Contents

1. Fluorescence lifetimes of MTFs

   Figure S1. Fluorescence decay profiles of (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_n$ MTFs

   Table S1. Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_n$ UTFs

   Figure S2. Fluorescence decay profiles of (MMT/BNMA@PVA)$_n$ MTFs.

   Table S2. Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA)$_n$ UTFs

2. Polarized fluorescence spectra of MTFs

   Figure S3. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_n$ MTFs

   Figure S4. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_{16}$ MTFs

   Figure S5. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_{24}$ MTFs

   Figure S6. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA)$_n$ MTFs

   Figure S7. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA)$_{16}$ MTFs

   Figure S8. Polarized fluorescence and the anisotropy value ($r$) for (MMT/BNMA@PVA)$_{24}$ MTFs
1. Fluorescence lifetimes of MTFs

Figure S1 and Figure S2 show fluorescence decay profiles of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs and (MMT/BNMA@PVA)_n MTFs, respectively. Owing to the difficulty in providing an appropriate interpretation of the multi-exponential decay curves (Formula 1), an average lifetime was calculated by using the formula 2\(^{[1, 2]}\). The inset of Figure S2 indicates the lifetimes of (MMT/BNMA@PVA)_n MTFs increasing with deposited cycles in a linear relationship. The lifetimes of MTFs are shown in Table S1, S2.

\[
y = y_0 + A_1 e^{-x/\tau_1} + A_2 e^{-x/\tau_2} \quad (1)
\]

\[
\tau_{av} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad (2)
\]


[3] \(\tau\): the fluorescence lifetime; \(\chi^2\): the fitting goodness.
Table S1. Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs

<table>
<thead>
<tr>
<th>Layer number</th>
<th>8</th>
<th>16</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifetime (ns)</td>
<td>13.81</td>
<td>14.51</td>
<td>17.02</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.9995</td>
<td>0.9994</td>
<td>0.9985</td>
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</table>

Table S1. Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA/LDHs/BNMA@PVA)_n MTFs

Figure S2. Fluorescence decay profiles of (MMT/BNMA@PVA)_n MTFs. The inset indicates the lifetimes of MTFs increasing with deposited cycles adding.

Table S2. Fluorescence lifetime and parameters of multi-exponential fit to the fluorescence decay of (MMT/BNMA@PVA)_n UTFs

<table>
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<th>Layer number</th>
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<th>16</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lifetime (ns)</td>
<td>4.57</td>
<td>11.23</td>
<td>15.82</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>0.9989</td>
<td>0.9980</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

2. Polarized fluorescence spectra of MTFs
To further investigate the orientation of BNMA between the LDHs and MMT nanosheets in the as-prepared MTFs, the fluorescence anisotropy value $r$ were obtained by the polarized fluorescence measurements$^{[4,5]}$. Two typical measurements of polarized fluorescence (glancing and normal incidence geometry as shown in Figure S4, Figure S5 and Figure S6) were used to determine the $r$ value. It was observed that, the (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_n$ MTFs show green photoluminescence with the anisotropic value ($r$) of -0.10~0.00 which differs from those results of most inorganic/organic hybrid materials via layer-by-layer assembly method. One of the important factors of these results is that BNMA are small functional molecules whose anisotropy of molecular structure is relatively low. At the same time, the long chain of PVA provides a flexible and soft micro-environment, therefore, leading to reduced anisotropy. Contrast with (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_n$ MTFs, (MMT/BNMA@PVA)$_n$ MTFs also show green photoluminescence and the anisotropic value ($r$) were negative and their absolute value were also small (Figure S7, Figure S8 and Figure S9). The uniform $r$ value indicates the thickness imposes no obvious influence on the macroscopic polarized luminescence characteristics with different bilayers throughout the whole assembly process.

$^{[4]}$ Valeur B. Molecular fluorescence: Principles and applications. Wiley-VCH, VerlagGmbH, 2001. $r$ can be expressed as the formula: $r = (I_{VV} - GI_{VH})/(I_{VV} + 2GI_{VH})$, where $G = I_{HV}/I_{HH}$, determined from the aqueous solution. $I_{VH}$ stands for the photoluminescence intensity obtained with vertical polarization excitation and horizontal polarization detection, and $I_{VV}, I_{HV}, I_{HH}$ are defined in a similar way.

Figure S3. Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_8$ MTFs.

Figure S4. Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_{16}$ MTFs.
Figure S5. Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_{24}$ MTFs

Figure S6. Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA)$_{8}$ MTFs
Figure S7 Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA)$_{16}$ MTFs

Figure S8. Polarized fluorescence profiles and the anisotropy value ($r$) for (MMT/BNMA@PVA/LDHs/BNMA@PVA)$_{24}$ MTFs