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Many exciplex systems exhibit organic long-persistent luminescence

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Abstract: Organic long-persistent luminescence (OLPL) is long-lasting luminescence from a photo-generated intermediated state, such as a charge separated state. Here, we show that many exciplex systems exhibit OLPL and that emission pathways of OLPL can be controlled by the relationship among local excited states and charge-transfer excited states of materials.

35 1. Introduction

36 Glow-in-the-dark materials exhibit continuous photoemission for a very long time. This
37 long-lasting emission can originate as radioluminescence, photoluminescence, or
38 chemiluminescence. Radioluminescent material has been known since the 20th century and was
39 used for glow-in-the-dark paints because it emits continuously without photoexcitation.^[1,2]
40 However, because it contains radioactive elements, radioluminescent glow-in-the-dark material
41 has gradually been replaced by long-persistence luminescent (LPL) materials based on
42 photoluminescence.^[1,2]

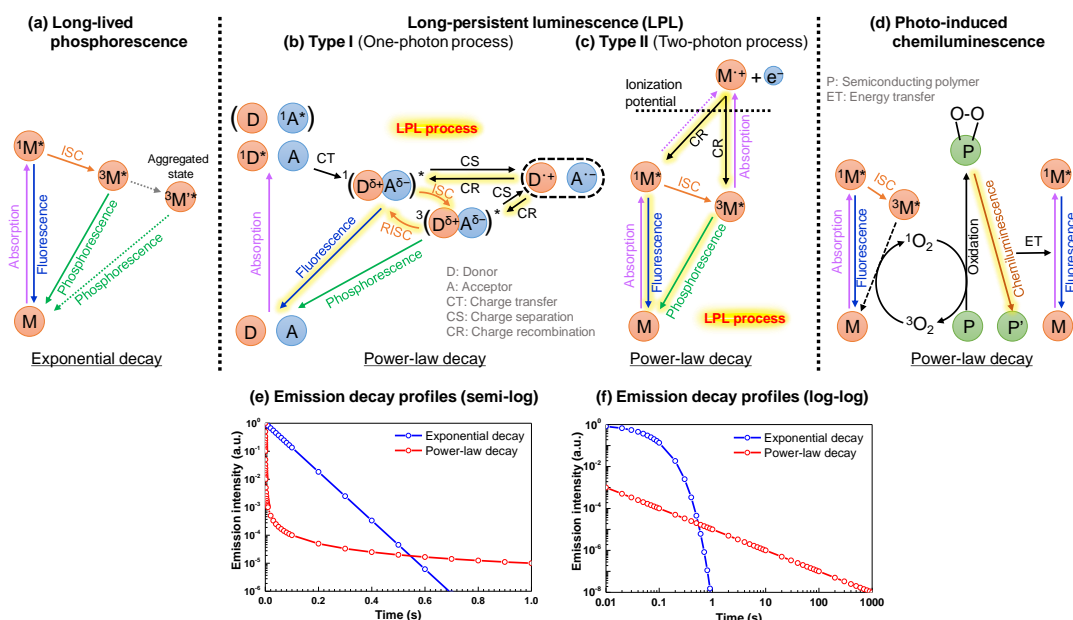
43 High-performance, LPL materials were developed in the mid 1990s, and are widely used for
44 emergency lights and watches.^[1-3] LPL systems all employ inorganic materials, and most of the
45 high-performance materials require rare earth elements.^[1-3] Moreover, inorganic materials
46 generally require high fabrication temperatures.^[1-3] Since inorganic LPL materials have no
47 flexibility, they are dispersed into polymer media in large-scale applications.

48 The above problems can be solved by using organic light-emitting materials.
49 Chemiluminescence results from a chemical reaction, and emission continues as long as the
50 energy source molecule (usually organic peroxide) remains available.^[4] Chemiluminescence
51 systems comprising energy source molecules and organic emitters have been commercialized
52 as chemical lights. Recently, a method for generating energy source peroxide species by photo-
53 oxidation of semiconducting polymers has been reported, and it has been used for bioimaging
54 (Figure 1).^[4] However, chemiluminescent systems cannot sustain long-term use due to
55 consumption of energy source agents.

56 Most organic photoluminescent materials showing long-lived emissions originate from
57 phosphorescent materials. Although phosphorescence is often quenched by competing
58 nonradiative processes, many organic systems having long-lived phosphorescence at room
59 temperature have been reported.^[5-10] However, phosphorescent emitters always exhibit
60 exponential decay since there is no energy storage mechanism (Figure 1). In contrast, most LPL

61 systems exhibit power-law decay due to the presence of an intermediate charged state.
 62 Moreover, LPL duration is related to photo-excitation time because of a charge-storage
 63 mechanism, but normal phosphorescence does not depend on the photo-excitation time.^[10]

64 The very first LPL emission from organic molecules was realized by dispersing an emitter
 65 molecule in a low-temperature polymer matrix under strong photo-excitation (Figure 1 (c)).^[11]
 66 The emitter exhibits photo-induced ionization because of second photon absorption from the
 67 excited states. The slow charge recombination exhibits LPL emission from both singlet and
 68 triplet excited states. However, this successive two-photon ionization process requires high
 69 excitation power and a low-temperature environment.^[12]



70
 71 **Figure 1.** Classification of long-lasting emission from organic molecules. Power-law emission decay is essential
 72 for long-lasting emission over several minutes, as in commercial inorganic LPL systems. (a) Long-lived
 73 phosphorescence: emission from photo-generated triplet excited states (or lower triplet states generated by
 74 aggregation) to singlet ground states. (b) Long-persistent luminescence by one-photon absorption: emission from
 75 intermediate charge-separated states. Because the charge recombination process is a second order reaction,
 76 emission follows power-law decay. (c) Long-persistent luminescence by two-photon absorption: successive two-
 77 photon absorption ionizes the emitter. The recombination of electron and ionized molecule exhibits LPL emission.
 78 (d) Photo-induced chemiluminescence: A photo-sensitizer generates singlet oxygen and causes photo-oxidation of

79 a semiconducting polymer. Bond dissociation exhibits continuous chemiluminescence.. Semi-log (e) and log-log
80 (f) plots of emission decay profiles.

81
82 Recently, we developed another organic LPL (OLPL) system exhibiting one-photon
83 ionization, by mixing an electron donor *N,N,N',N'*-tetramethylbenzidine (TMB) and an electron
84 acceptor 2,8-bis(diphenylphosphoryl)dibenzo[b,d]thiophene (PPT) (Figure 1 (b)).^[13-15] After
85 photo-excitation of this OLPL system, an intermediate charge-separated state is generated by
86 charge transfer from the electron donor to the acceptor. After turning off the photoexcitation,
87 continuous charge-recombination produces LPL having a power-law emission decay.^[16] This
88 OLPL system can be fabricated not only using a low-temperature melt-casting method, but also
89 thermal evaporation and spin-coating methods.^[17] Moreover, the emission color of OLPL can
90 be controlled by tuning the highest occupied molecular orbital (HOMO) level of the donor or
91 energy transfer from exciplexes to extra-emitter dopants.^[15,18] Furthermore, a transparent and
92 flexible OLPL system can be realized by using a polymer-based acceptor.^[19]

93 However, reported OLPL systems are few in number and the material selection rule for
94 OLPL is still unclear. OLPL emission is based on exciplex, which is a transition from the lowest
95 unoccupied molecular orbital (LUMO) of the acceptor to the highest occupied molecular orbital
96 HOMO of the donor.^[20-22] Therefore, the emission color of an OLPL system can be tuned with
97 different combinations of donor and acceptor.^[15,20] We also demonstrated that the lowest triplet-
98 excited state of the donor significantly influences the emission mechanism.^[14]

99 In this report, we systematically investigated LPL performance and physical properties of
100 many donor and acceptor pairs, demonstrating the importance of the triplet-excited states of
101 both the donor and acceptor for LPL emission.

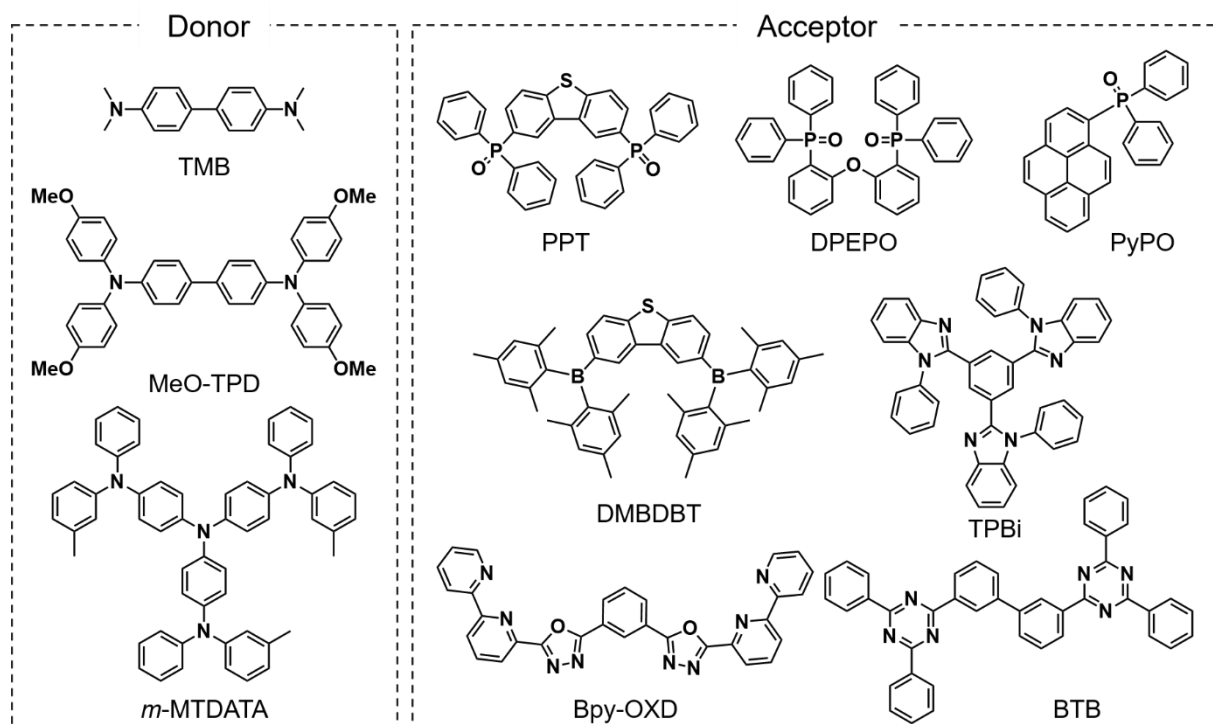


Figure 2. Chemical structures of electron donors and acceptors

2. Results and Discussion

2.1. Optical and electrical properties of electron donors and acceptors

Various electron donors and acceptors were investigated (Figure 2). TMB, 4,4',4''-tris[phenyl(*m*-tolyl)amino]triphenylamine (*m*-MTDATA), and *N,N,N',N'*-tetrakis(4-methoxyphenyl)benzidine (MeO-TPD) were used as donors and PPT, diphenyl(1-pyrenyl)phosphine oxide (PyPO), 2,8-bis(2,4,6-trimesitylboronic)dibenzo[*b,d*]thiophene (DMBDBT), 3,3'-bis(4,6-diphenyl-1,3,5-triazin-2-yl)-1,1'-biphenyl (BTB), 1,3-bis[2-(2,2'-bipyridine-6-yl)-1,3,4-oxadiazole-5-yl]benzene (Bpy-OXD), 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi), and bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) were used as acceptors. Ultraviolet-visible (UV-Vis) absorption, fluorescence, and phosphorescence spectra of these materials are shown in Figure S1. Energy levels of the lowest triplet-excited states (T_1) were calculated from onsets of phosphorescence spectra obtained at 77 K. HOMO and LUMO levels were determined from the first oxidation or reduction peaks of cyclic voltammograms or differential-pulse voltammograms (Figure S2; Table 1).

118

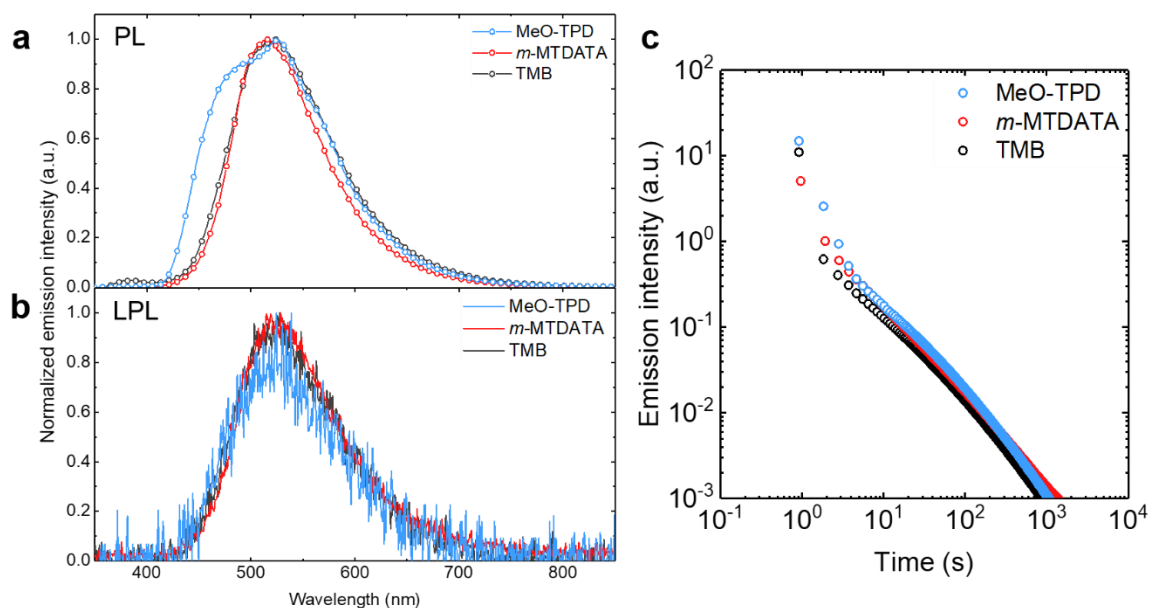
119 **Table 1.** Optical properties of donors, acceptors, and exciplexes

Donor	Acceptor	HOMO (Donor) [eV] ^a	LUMO (Acceptor) [eV] ^a	$\Delta E_{\text{HOMO-LUMO}}$ [eV]	¹ CT [eV] ^b	³ LE _D [eV] ^c	³ LE _A [eV] ^c	$E(^3\text{LE}_D-^1\text{CT})$ [eV]	$E(^3\text{LE}_A-^1\text{CT})$ [eV]	PL peak [nm] ^d	LPL peak [nm] ^d	Φ_{PL} [%]	LPL duration time [s] ^e
TMB	PPT	-4.65	-1.68	2.97	2.78	2.56	3.08	-0.22	0.30	522	527	6.5	868
MeO-TPD	PPT	-4.83	-1.68	3.15	2.94	2.56	3.08	-0.38	0.14	493(Sh), 523	524	9.3	1073
<i>m</i> -MTDATA	PPT	-4.58	-1.68	2.90	2.74	2.76	3.08	0.02	0.34	516	523	35.2	1352
<i>m</i> -MTDATA	TPBi	-4.58	-1.84	2.74	2.70	2.76	2.80	0.06	0.10	546	557	16.6	110
<i>m</i> -MTDATA	DMBDBT	-4.58	-2.05	2.53	2.68	2.76	3.00	0.08	0.32	525	N.D.	40.2	11
<i>m</i> -MTDATA	PyPO	-4.58	-2.20	2.38	2.85	2.76	2.08	-0.09	-0.77	501	N.D.	52.1	N.D.
<i>m</i> -MTDATA	Bpy-OXD	-4.58	-2.35	2.37	2.57	2.76	2.82	0.19	0.25	568	587	10.9	47
<i>m</i> -MTDATA	BTB	-4.58	-2.32	2.26	2.48	2.76	3.01	0.28	0.53	575	N.D.	12.7	15
<i>m</i> -MTDATA	DPEPO	-4.58	-1.54	3.04	3.03	2.76	3.52	-0.27	0.49	436	471	7.6	229

a. Calculated from redox peaks of cyclic voltammogram; b. Calculated from the onset of the exciplex emission spectra; c. Calculated from the phosphorescence spectra obtained at 77 K; d. Obtained from Figure S3; e. Time until the emission intensity drops below 3 pW.

120

121 Mixed films with a 1:99 molar ratio of donor/acceptor were fabricated using a melt-cast
 122 method, from which steady-state photoluminescence and LPL spectra, emission decay profiles,
 123 and emission quantum yields (Φ_{PL}) were obtained (Figures 3 and 4). In this study, the ³CT level
 124 of exciplex is assumed from the ¹CT level of exciplex obtained at the onset of steady-state
 125 photoluminescence spectra, because there is no method to measure the ³CT of exciplex directly.
 126 Many exciplex systems have very small energy gap between the ¹CT and the ³CT because the
 127 HOMO is localized on donor and LUMO is localized on acceptor, which lead to small exchange
 128 energy.^[20]



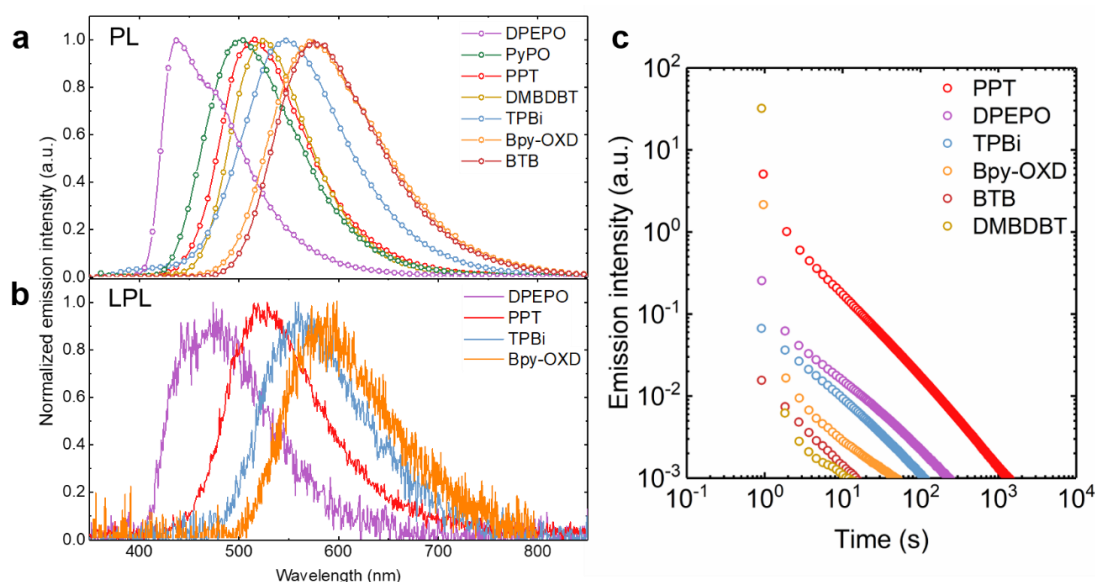
129
 130 **Figure 3.** PL (a) and LPL (b) spectra and LPL emission decay (c) of MeO-TPD/PPT, *m*-MTDATA/PPT, and
 131 TMB/PPT. Charge transfer (CT) emission corresponding to $\Delta E_{\text{HOMO-LUMO}}$. LPL spectra was changed when ${}^3\text{LE}_D$
 132 is much lower than ${}^1\text{CT}$ (MeO-TPD/PPT).

133 2.2. Donor-dependence of LPL performance

134 When PPT was used as the acceptor, all films (TMB/PPT, *m*-MTDATA/PPT, and MeO-
 135 TPD/PPT) exhibited broad exciplex emission, corresponding to a transition from LUMO of the
 136 acceptor to HOMO of the donor (Figure 3). Because the TMB/PPT and *m*-MTDATA/PPT films
 137 have almost the same energy gap between donor HOMO and acceptor LUMO ($\Delta E_{\text{HOMO-LUMO}}$
 138 = 2.97 and 2.90 eV, respectively), both films exhibited similar photoluminescence and LPL
 139 spectra. However, the *m*-MTDATA/PPT system exhibited $\sim 1.5\times$ longer emission because its
 140 Φ_{PL} was higher than that of TMB/PPT. Similar correlations between the Φ_{PL} and LPL duration
 141 have been reported in previous reports^[15,18]. Because the MeO-TPD/PPT film had a larger
 142 energy gap ($\Delta E_{\text{HOMO-LUMO}} = 3.15$ eV), it exhibited two emission peaks at 493 nm (shoulder
 143 peak) and 523 nm in the steady-state photoluminescence spectrum and a single peak at 523 nm
 144 in the LPL spectrum. Because the LPL spectrum corresponds to the phosphorescence of MeO-
 145 TPD (Figure S3), the PL peak at 493 nm represents the exciplex emission between MeO-TPD

146 and PPT. However, the LPL decay of MeO-TPD follows power-law decay unlike conventional
 147 phosphorescence emitters showing exponential decay.

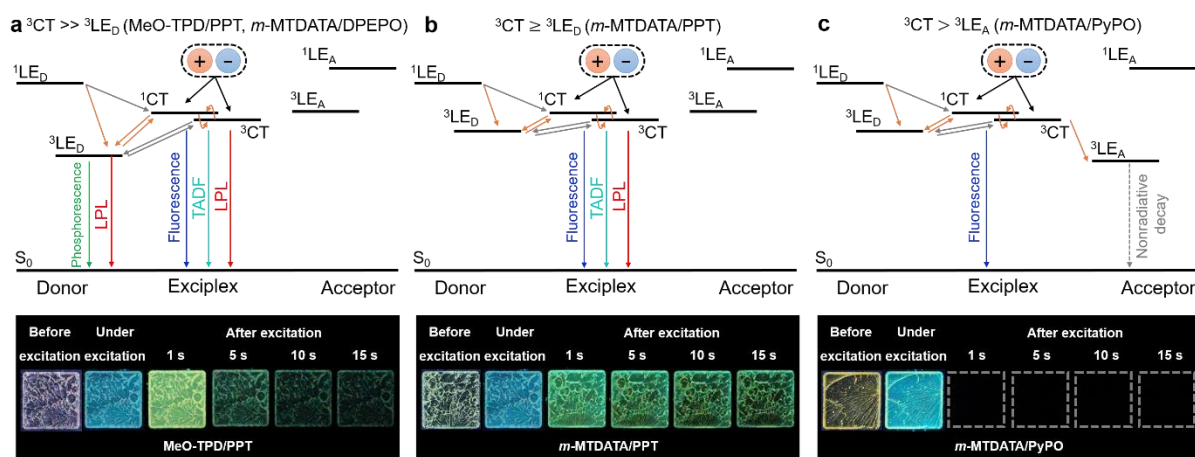
148 The LPL of MeO-TPD/PPT can be explained by electron transfer in the triplet-excited states
 149 (Figure 5). In the case of TMB/PPT and *m*-MTDATA/PPT systems, the energy gap between
 150 the ^1CT and the lowest triplet-excited state of the donor ($^3\text{LE}_\text{D}$), $\Delta E(^1\text{CT} - ^3\text{LE}_\text{D})$, is very small
 151 (0.22 and -0.02 eV, respectively) (Figure S4). Therefore, the reverse intersystem crossing
 152 (RISC) from $^3\text{LE}_\text{D}$ to ^1CT is efficient, as in thermally activated delayed fluorescence (TADF)
 153 molecules.^[23-26] As a result, excitons generated by charge recombination are mainly populated
 154 on the ^1CT and exhibit LPL from the exciplex. In contrast, MeO-TPD/PPT has a rather large
 155 energy gap between $\Delta E(^1\text{CT} - ^3\text{LE}_\text{D}) = 0.38$ eV, which almost prevents the RISC process.
 156 Therefore, both transitions from ^1CT and $^3\text{LE}_\text{D}$ are present in PL (Figure S5). After charge
 157 recombination, excitons populate mainly $^3\text{LE}_\text{D}$ through electron transfer and exhibit LPL
 158 emission from $^3\text{LE}_\text{D}$. $^3\text{LE}_\text{D}$ is usually emissive in OLPL system because the donor molecule is
 159 isolated in a rigid acceptor matrix having high triplet energy.^[10] Therefore, a small $\Delta E(^1\text{CT} -$
 160 $^3\text{LE}_\text{D})$ is required for efficient LPL emission.



161
 162 **Figure 4.** PL (a) and LPL (b) spectra and LPL emission decay (c) of *m*-MTDATA/Acceptor (DPEPO, PPT,
 163 DMBDBT, PyPO, TPBi, Bpy-OXD, and BTB). Sky-blue to orange exciplex emission was observed,
 164 corresponding to various $\Delta E_{\text{HOMO-LUMO}}$.

165 **2.3. Acceptor-dependence of LPL performance**

166 Subsequently, when *m*-MTDATA was used as the donor, all combinations of *m*-
 167 MTDATA/Acceptor (DPEPO, PPT, DMBDBT, PyPO, TPBi, Bpy-OXD, and BTB) exhibited
 168 exciplex emission (Figure 4). Sky-blue to orange exciplex emission was observed
 169 corresponding to various $\Delta E_{\text{HOMO-LUMO}}$ of donor and acceptor combinations. Emission decay
 170 profiles of all films except *m*-MTDATA/PyPO follow power-law decay, which is characteristic
 171 of LPL emission. LPL spectra of *m*-MTDATA/DMBDBT and *m*-MTDATA/BTB are not
 172 presented in Figure 4b, since their LPL intensities were too weak to be detected.



173 **Figure 5.** Proposed emission mechanism and photograph of OLPL (a) When ${}^3\text{CT} \gg {}^3\text{LE}_D$. (b) ${}^3\text{CT} \geq {}^3\text{LE}_D$ (c)
 174 ${}^3\text{CT} > {}^3\text{LE}_A$. Energy level relationships among ${}^3\text{LE}_A$, ${}^3\text{LE}_D$, and ${}^1\text{CT}$ are important to control the emission pathway
 175 after charge recombination.
 176

177
 178 In the case of the *m*-MTDATA/PyPO system, LPL emission was quenched by electron
 179 transfer because the triplet energy level of PyPO (${}^3\text{LE}_A$) is much lower than that of the exciplex
 180 (${}^3\text{CT}$). Excitons generated by charge recombination are transferred to the non-emissive ${}^3\text{LE}_A$
 181 state.

182 The *m*-MTDATA/DPEPO system shows spectral changes between PL and LPL spectra
 183 similar to those of the MeO-TPD/PPT system (Figure S6). Because ${}^3\text{LE}_D$ is lower than ${}^1\text{CT}$,
 184 LPL is mainly obtained from ${}^3\text{LE}_D$. Notably, the *m*-MTDATA/DMBDBT system exhibits

185 strong degradation during photo-excitation (Figure S7). The unstable radical anion of
186 DMBDBT might cause this photo-degradation after the charge-separation process.

187 These results identify several important factors for developing efficient OLPL systems.
188 When the energy level of ^1CT is lowest or slightly higher (< 0.3 eV) than that of $^3\text{LE}_\text{D}$ and $^3\text{LE}_\text{A}$,
189 the mixture of donor and acceptor exhibits LPL from ^1CT (fluorescence-based LPL). When
190 $^3\text{LE}_\text{D}$ is enough lower than ^1CT , LPL emission is mainly obtained from emissive $^3\text{LE}_\text{D}$, since
191 the donor is in a rigid acceptor matrix (phosphorescence-based LPL). When $^3\text{LE}_\text{A}$ is lowest,
192 LPL is quenched because $^3\text{LE}_\text{A}$ is usually non-emissive due to competing nonradiative decay.
193 When LPL emission is obtained from the exciplex, LPL emission color corresponds to the
194 $\Delta E_{\text{HOMO-LUMO}}$ and emission intensity corresponds to Φ_{PL} of the exciplex. The radical cation state
195 of donors and the radical anion state of acceptors must be stable to avoid photo-decomposition.

196 3. Conclusions

197 In conclusion, we demonstrated that many exciplex systems exhibit LPL emission. The
198 emission color of OLPL corresponds to the energy gap between donor HOMO and acceptor
199 LUMO. To design efficient OLPL systems, energy level relationships among $^3\text{LE}_\text{A}$, $^3\text{LE}_\text{D}$, and
200 ^1CT are important for controlling the emission pathway after charge recombination. Φ_{PL} of the
201 exciplex and redox stabilities of the materials are also key factors. This information will enable
202 development of efficient, full-color OLPL systems involving not only small molecules, but also
203 polymers.

204 205 Experimental Section

206 **Materials:** PPT [27], DPEPO [28], PyPO [29], DMBDBT [30], and BTB [31] were prepared as
207 described in the literature, while TMB, MeO-TPD, *m*-MTDATA, TPBi and Bpy-OXD were
208 obtained from TCI Chemicals (Tokyo, Japan) or Luminescence Technology Corp. (Taipei,
209 Taiwan) and purified by sublimation.

210 **Film fabrication:** In a nitrogen-filled glovebox, mixtures of donors and acceptors were placed
211 on template glass substrates with a surface area of 100 mm² and a depth of 0.5 mm, whereupon
212 they were heated to 250° C for 10 s. After melting, substrates were rapidly cooled to room
213 temperature.

214 **Optical and electrical Measurements:** Absorption spectra were measured using a UV-vis-
215 NIR spectrophotometer (LAMBDA 950, Perkin Elmer). Photoluminescence spectra were
216 measured using spectrofluorometers (FluoroMax, Horiba Jobin Yvon; FP-8600, JASCO; and
217 PMA-12, Hamamatsu Photonics). Absolute photoluminescence quantum yields (Φ_{PL}) were
218 measured using an integrating sphere with a photoluminescence measurement unit
219 (Quantaaurus-QY, Hamamatsu Photonics).

220 Cyclic voltammetry measurements were carried out using an electrochemical analyzer
221 (Model 608D+DPV, BAS). Measurements were performed in dried and oxygen-free DMF
222 using 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. A platinum
223 fiber was used as a counter electrode, with glassy carbon as a working electrode, and Ag/Ag⁺
224 as a reference electrode. Redox potentials were referenced against ferrocene/ferrocenium
225 (Fc/Fc⁺). Corresponding LUMO energies were calculated from reduction peaks using an
226 absolute value of -4.8 eV to vacuum for the Fc/Fc⁺ redox potential.

227 **LPL Measurements:** LPL properties (spectra and decay profiles) were obtained using a
228 measurement system in a glove box. Fabricated films were placed in the dark box and excited
229 using a 340-nm LED (M340L4, Thorlabs) with a band pass filter (340 ± 5 nm) at a fixed
230 excitation power (100 μW cm⁻²). PL and LPL spectra were recorded using a multichannel
231 spectrometer (QE-Pro, Ocean Photonics). Emission decay profiles were obtained without
232 wavelength sensitivity calibration using a silicon photomultiplier (C13366-1350GA,
233 Hamamatsu Photonics) connected to a multimeter (34461A, Keysight).

234

235

236 **Supporting Information**

237 Supporting Information is available from the Wiley Online Library or from the author.

238

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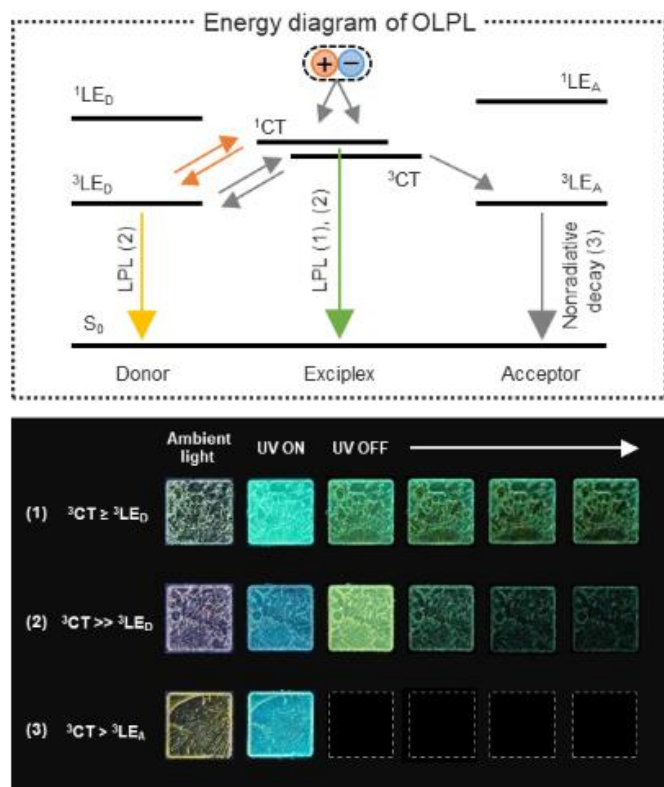
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293
 294 **Keyword** long-persistent luminescence, organic semiconductor, charge separation, charge
 295 recombination, exciplex

296
 297 Naohiro Nishimura, Zesen Lin, Kazuya Jinnai, Ryota Kabe*, and Chihaya Adachi*

298
 299 **Many exciplex systems exhibit organic long-persistence luminescence**

300
 301 ToC figure



302
 303 Organic long-persistent luminescence (OLPL) is long-lasting luminescence from a photo-
 304 generated intermediated state. Here, we show that many exciplex systems exhibit OLPL and
 305 that emission pathways of OLPL can be controlled by the relationship among local excited
 306 states (3LE_D and 3LE_A) and charge-transfer excited states (3CT) of materials.
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310 Supporting Information

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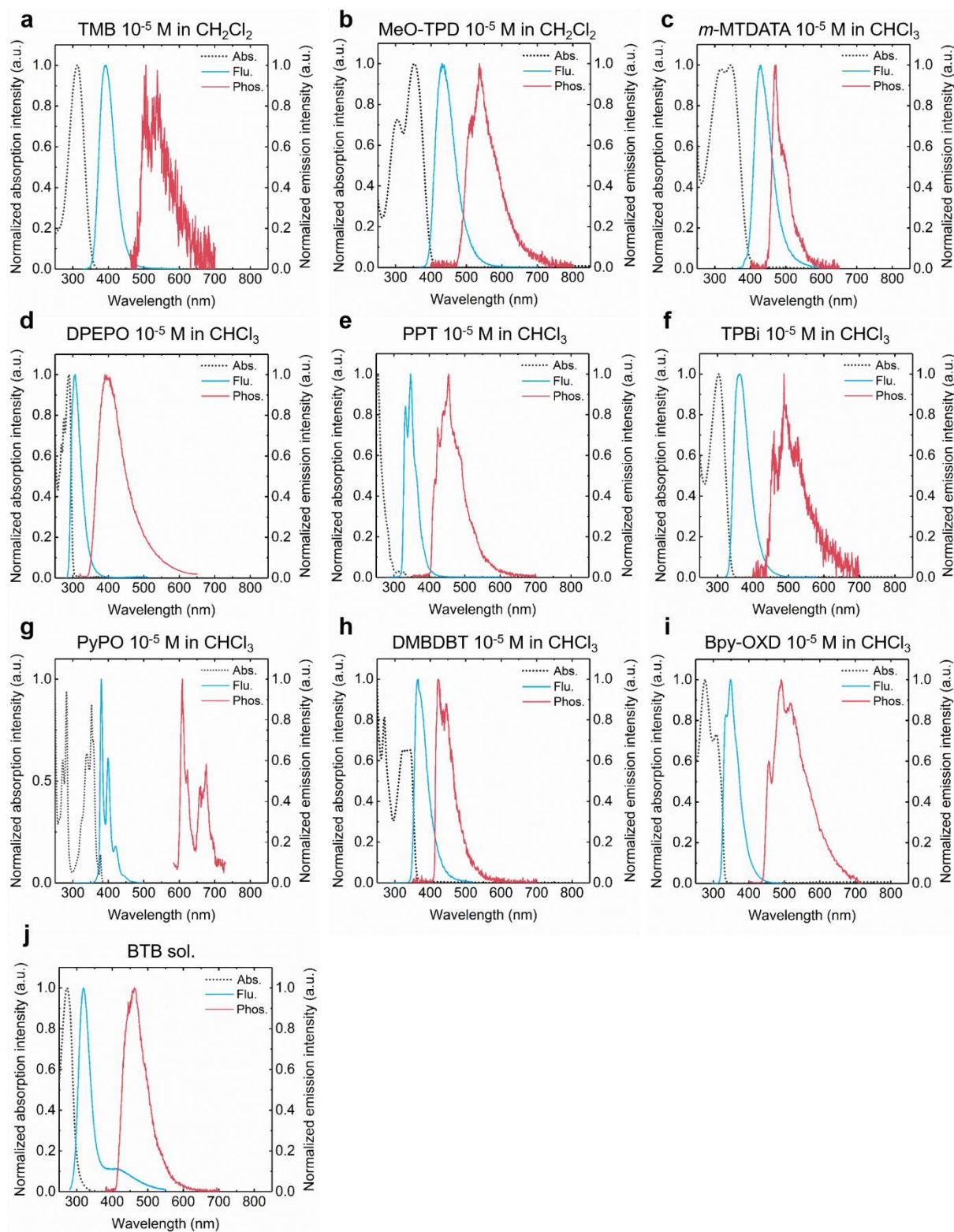
313 **Many organic exciplex systems exhibit long-persistence luminescence**

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315 *Naohiro Nishimura, Zesen Lin, Kazuya Jinnai, Ryota Kabe*, Chihaya Adachi**

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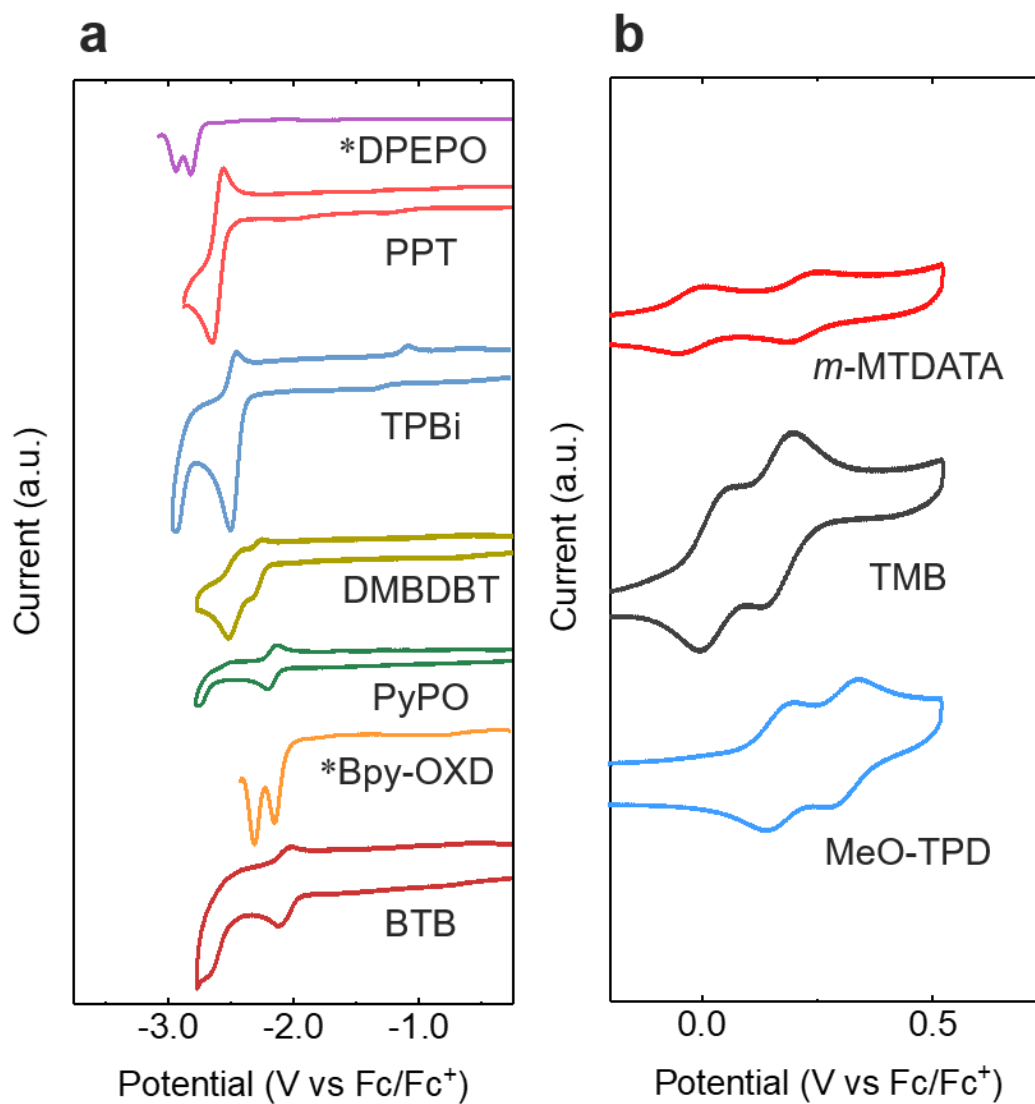
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319 **Figure S1.** Local excited energy levels of donors and acceptors ($^1\text{LE}_D$, $^3\text{LE}_D$, $^1\text{LE}_A$, and $^3\text{LE}_A$) were obtained

320 from solution-state emission spectra. UV-vis absorption, fluorescence, and phosphorescence spectra of the

321 donors and acceptors in solution. Phosphorescence spectra were obtained at 77 K.

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324 **Figure S2.** Donor HOMO and acceptor LUMO levels were calculated from cyclic voltammograms (or

325 *differential pulse voltammogram) of acceptors (a) and donors (b).

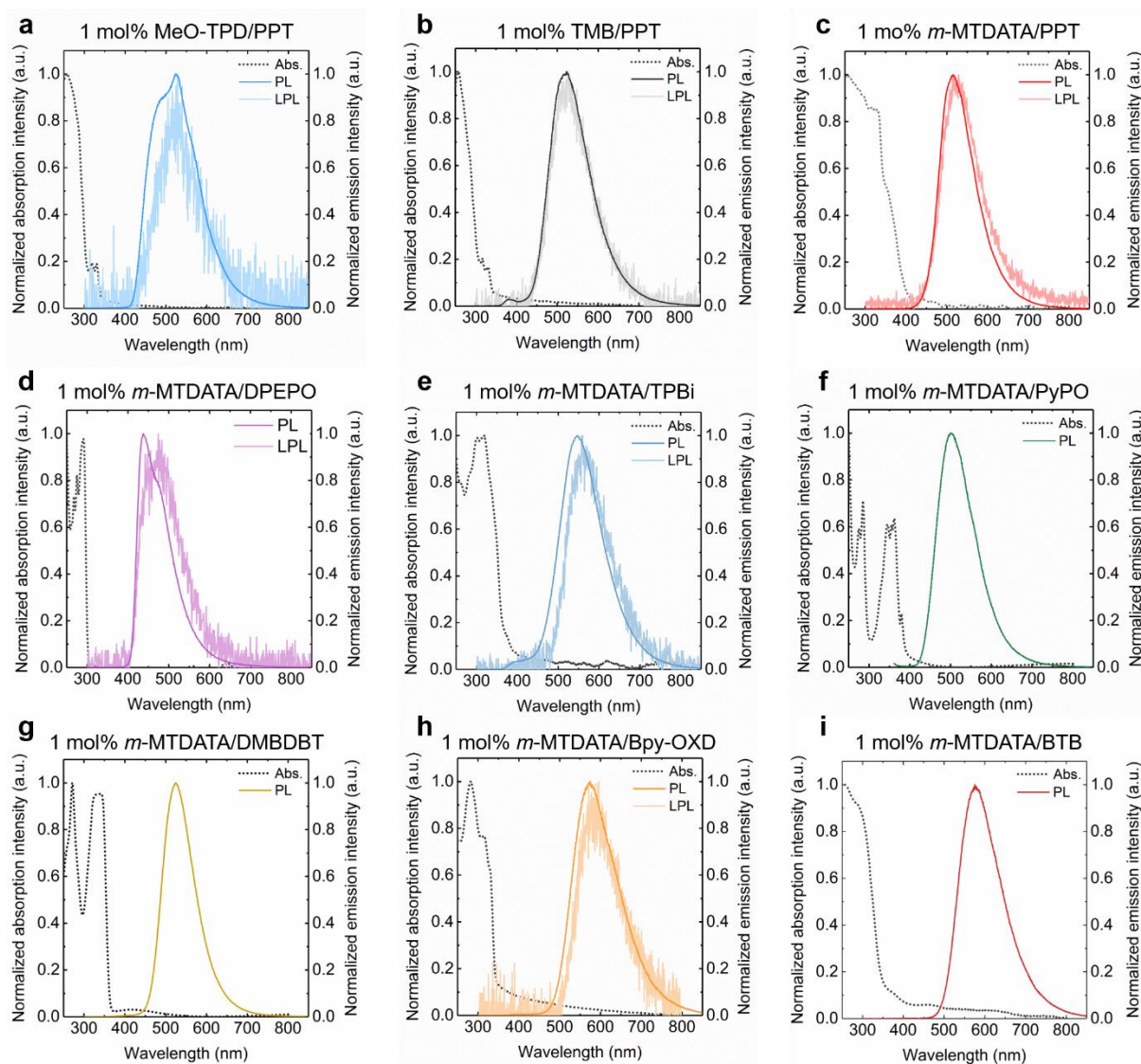


Figure S3. Comparison between steady-state photoluminescence (PL) and LPL spectra of all films. When $\Delta E(^1CT - ^3LE_D)$ is large, LPL spectra are changed from PL spectra (a,d). When $\Delta E(^1CT - ^3LE_D)$ is very small, PL and LPL spectra are almost identical (b,c,e,h). When $\Delta E(^1CT - ^3LE_A)$ is large, LPL is quenched (f). LPL intensities were too weak to be detected (g, i)

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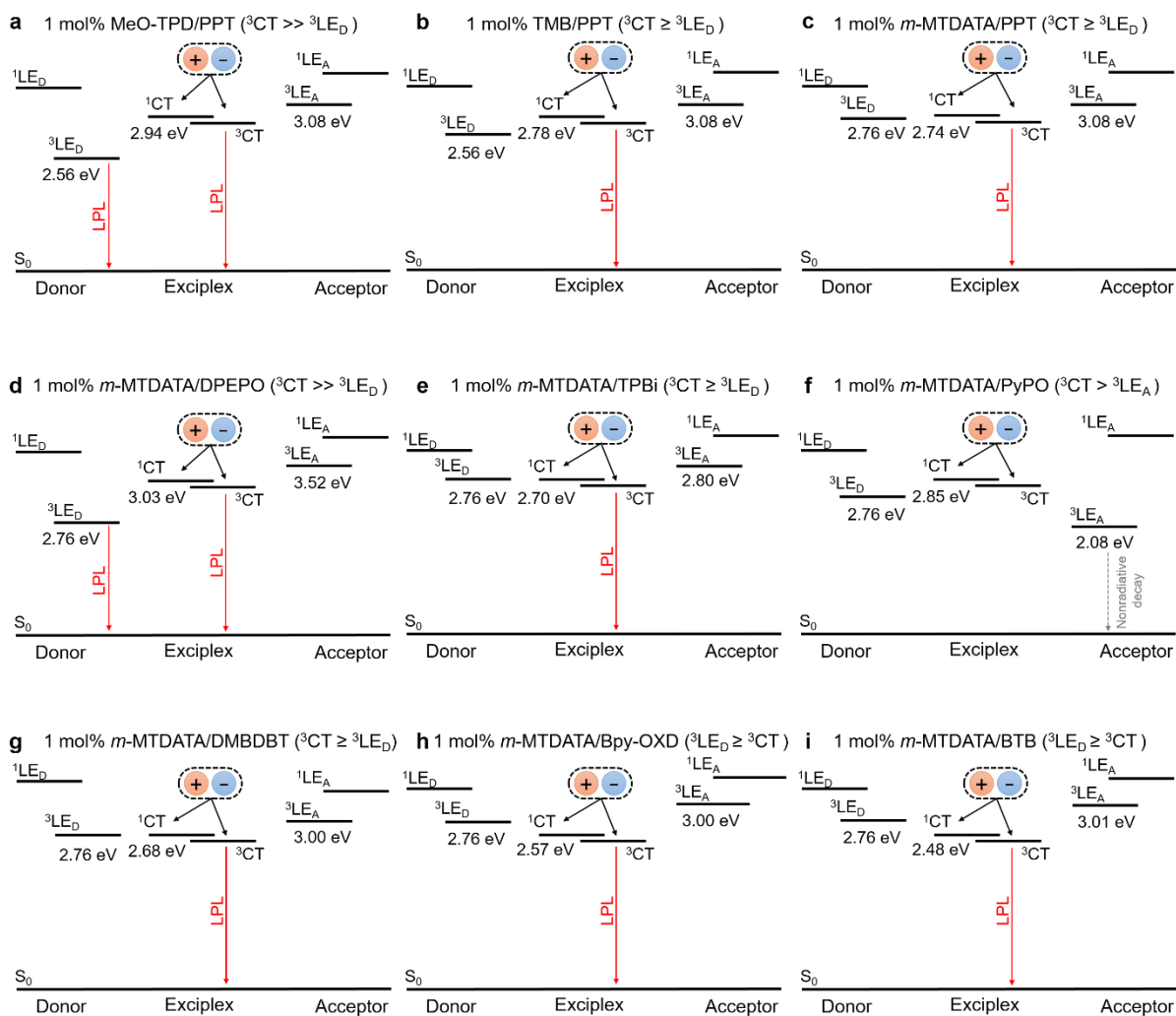
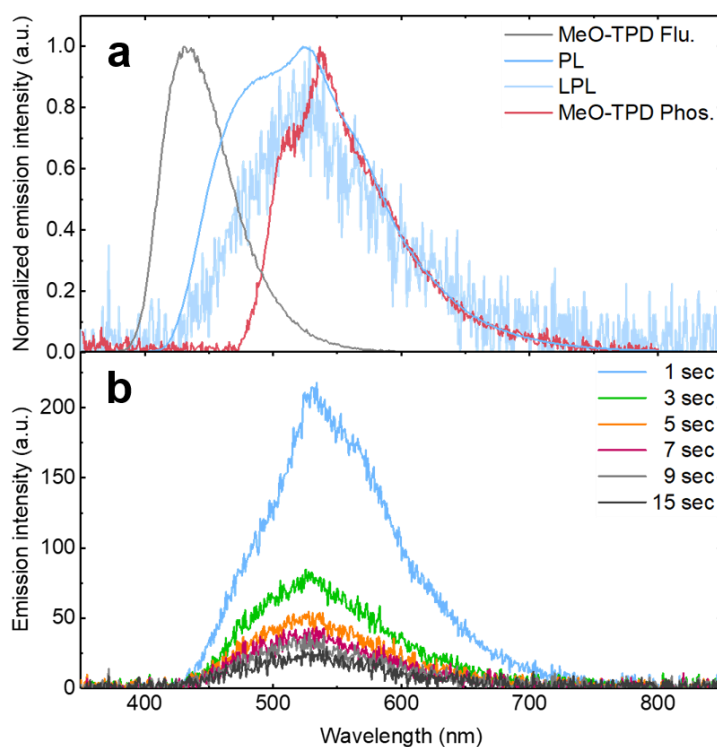


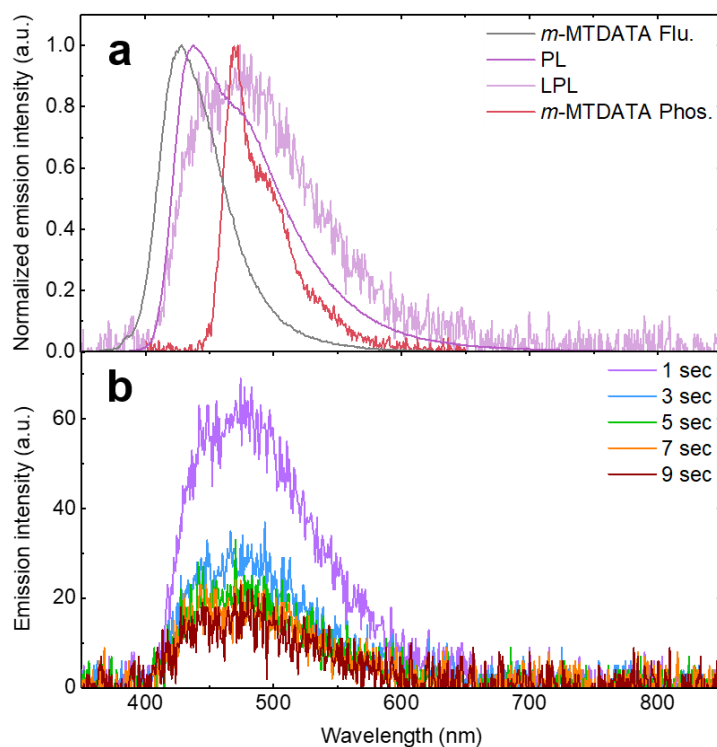
Figure S4. The energy-level-relationship for all the exciplex couples

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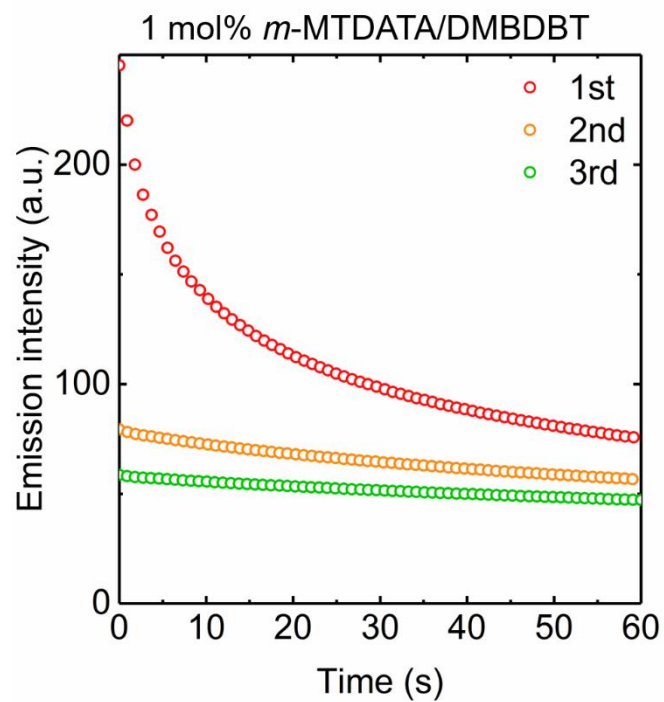
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 335 **Figure S5.** Time-dependent spectral shifting of an MeO-TPD/PPT film from PL (transition from $^3\text{LE}_D$ and ^1CT)
 336 to LPL (transition from ^1CT). (a) Fluorescence and phosphorescence spectra of MeO-TPD, and PL and LPL
 337 spectra of MeO-TPD/PPT film. (b) Time-dependent emission spectra of MeO-TPD/PPT film.



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 339 **Figure S6.** Time-dependent spectral shifting of a *m*-MTDATA/DPEPO film from PL (transition from $^3\text{LE}_D$ and
 340 ^1CT) to LPL (transition from ^1CT). (a) Fluorescence and phosphorescence spectra of *m*-MTDATA and PL and
 341 LPL spectra of *m*-MTDATA/DPEPO film. (b) Time-dependent emission spectra of a *m*-MTDATA/DPEPO film.



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Figure S7. Photo-degradation of a *m*-MTDATA/DMBDBT film. Emission intensity diminishes during photo-irradiation (60 s) of *m*-MTDATA/DMBDBT film with repeated measurements.