ELECTRONIC SUPPLEMENTARY INFORMATION

Ultrafast photoinduced electron transfer in face-to-face charge-transfer π-complexes of planar porphyrins and hexaazatriphenylene derivatives

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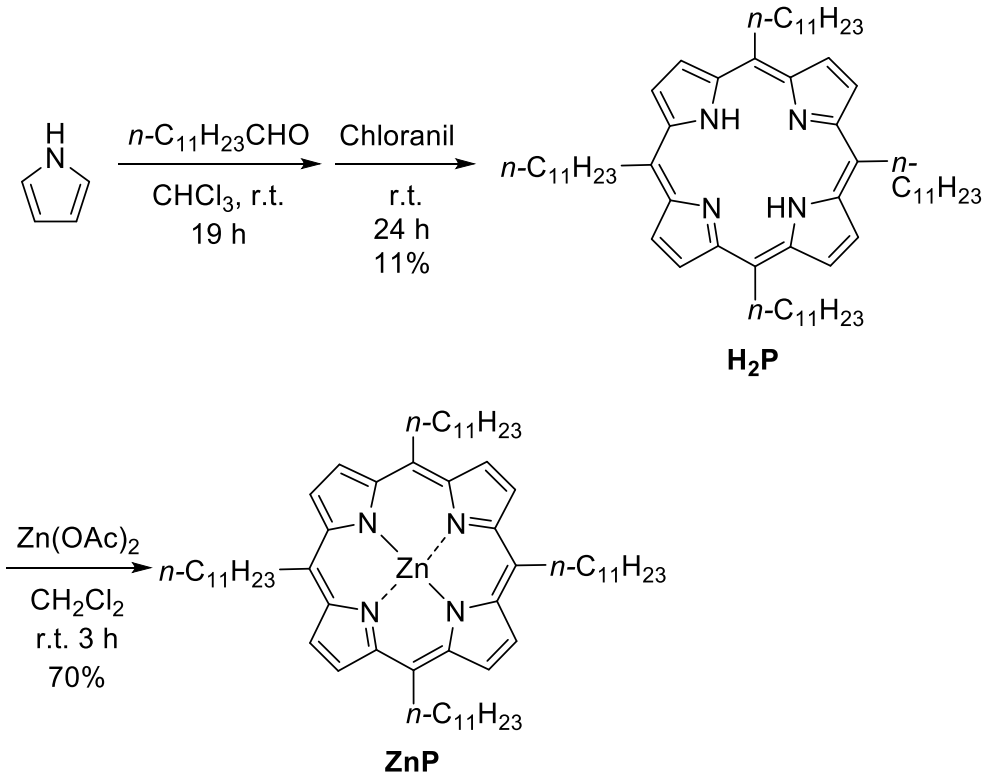
Experimental section

Femtosecond laser flash photolysis. Femtosecond transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses were derived from the fundamental output of Integra-C (λ = 786 nm, 2 mJ/pulse and fwhm = 130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into a second harmonic generation (SHG) unit: Apollo (Ultrafast Systems) for excitation light generation at λ = 393 nm, while the rest of the output was used for white light generation. The laser pulse was focused on a sapphire plate of 3 mm thickness and then white light continuum covering the visible region from λ = 410 nm to 800 nm was generated via self-phase modulation. A variable neutral density filter, an optical aperture, and a pair of polarizer were inserted in the path in order to generate stable white light continuum. Prior to generating the probe continuum, the laser pulse was fed to a delay line that provides an experimental time window of 3.2 ns with a maximum step resolution of 7 fs. In our experiments, a wavelength at λ = 393 nm of SHG output was irradiated at the sample cell with a spot size of 1 mm diameter where it was merged with the white probe pulse in a close angle (< 10°). The probe beam after passing through the 2 mm sample cell was focused on a fiber optic cable that was connected to a CMOS spectrograph for recording the time-resolved spectra (λ = 410 - 1600 nm). Typically, 1500 excitation pulses were averaged for 3 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. All measurements were conducted at room temperature.

Scheme S1 Synthetic schemes of H_2P and ZnP



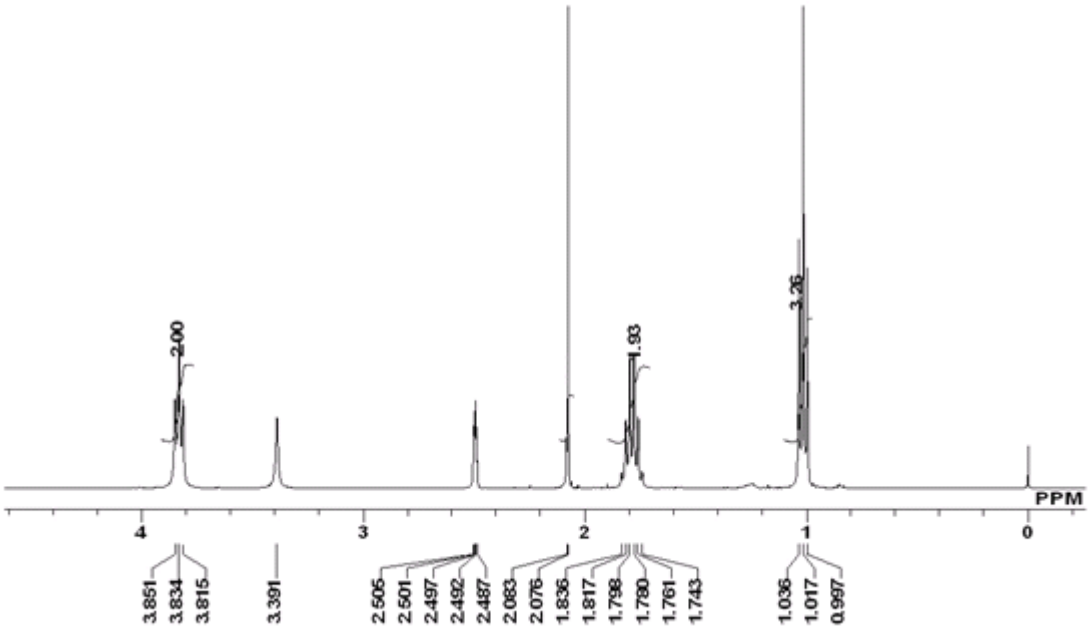


Fig. S1 ^{1}H NMR spectrum of C_3HAT-TIm in DMSO-d_6.

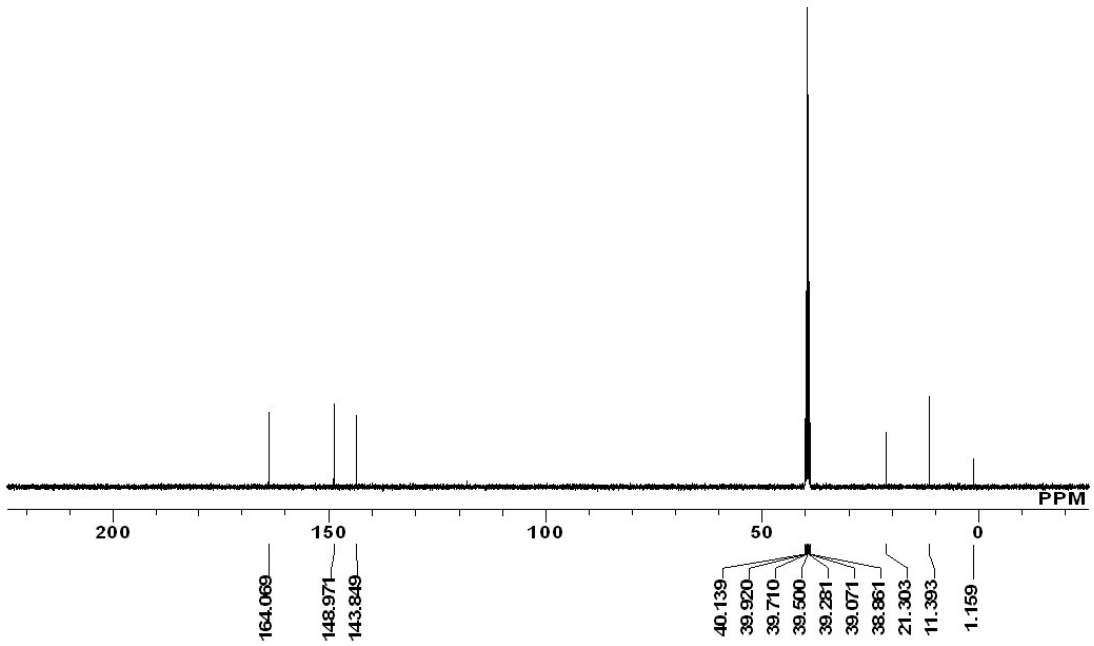


Fig. S2 ^{13}C NMR spectrum of C_3HAT-TIm in DMSO-d_6.

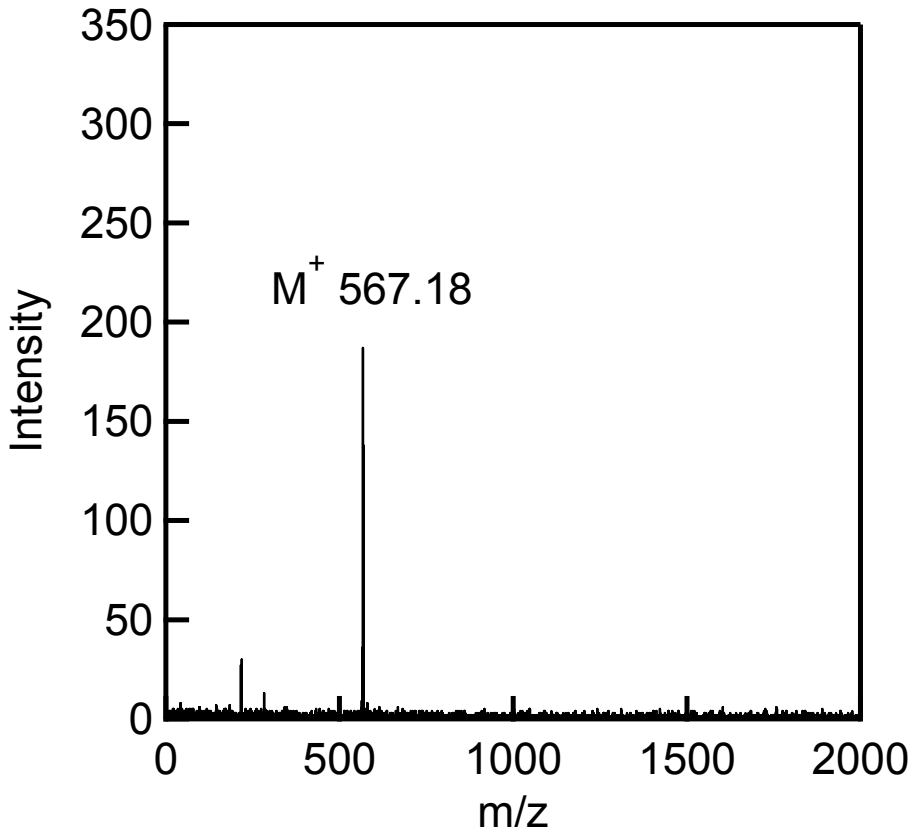


Fig. S3 MALDI-TOF mass spectrum of C_3HAT-TIm.

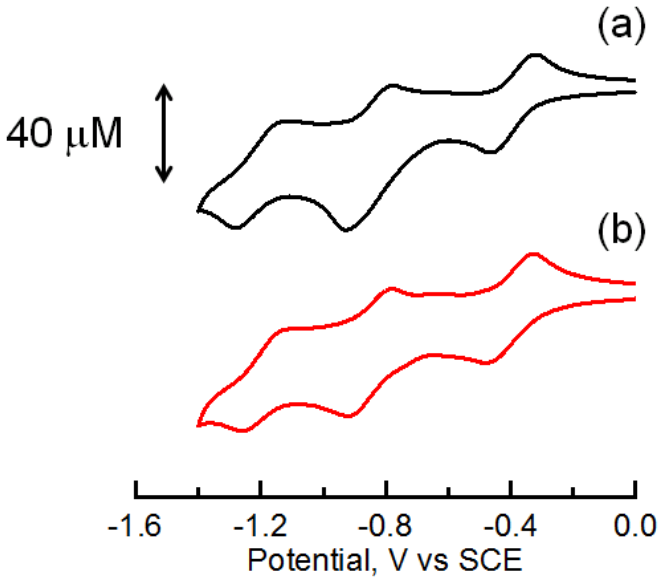


Fig. S4 Cyclic voltammograms of (a) C_3HAT-TIm and (b) C_{12}HAT-TIm in CH_2Cl_2 with 0.10 M $^nBu_4NPF_6$ as supporting electrolyte. Saturated calomel electrode (SCE) was used as a reference electrode. Scan rate: 0.1 V s^{-1}.

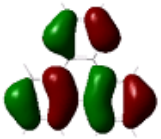
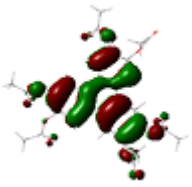
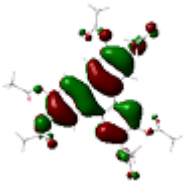
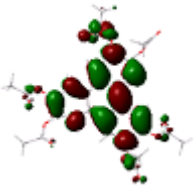
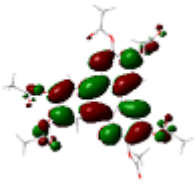
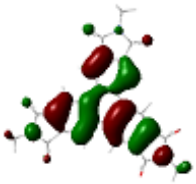
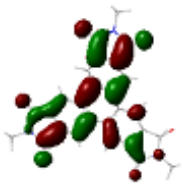
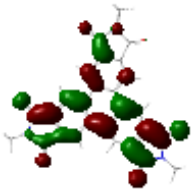
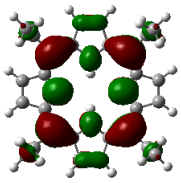
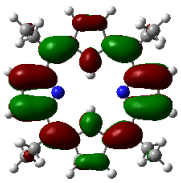
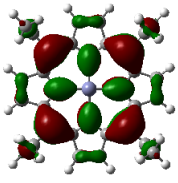
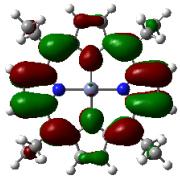
compound	HOMO−1	HOMO	LUMO	LUMO+1
TPh				
	−5.89 eV	−5.89 eV	−0.92 eV	−0.92 eV
TPhOAc				
	−6.23 eV	−6.20 eV	−1.54 eV	−1.52 eV
TPh-TIm				
	−7.31 eV	−7.31 eV	−3.25 eV	−3.25 eV
H_2P				
		−4.77 eV	−2.14 eV	
ZnP				
		−4.85 eV	−2.05 eV	

Fig. S5 Molecular orbitals and energy levels calculated in B3LYP/6-31+G(d) level of TPh and porphyrin derivatives.

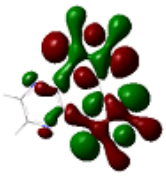
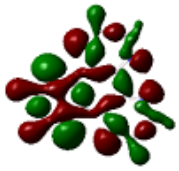
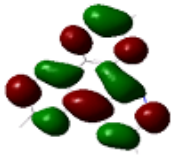
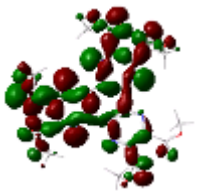
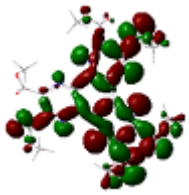
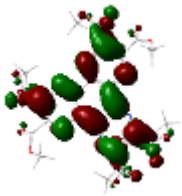
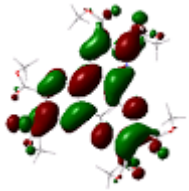
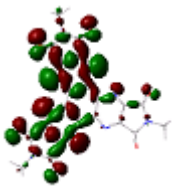
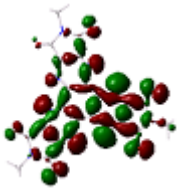
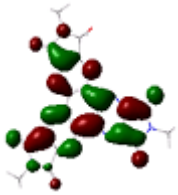
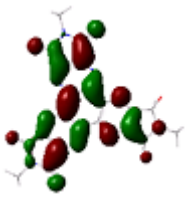
compound	HOMO−1	HOMO	LUMO	LUMO+1
HAT				
	−6.89 eV	−6.89 eV	−2.16 eV	−2.15 eV
$HAT(COOMe)_6$				
	−7.59 eV	−7.58 eV	−3.43 eV	−3.43 eV
HAT-TIm				
	−7.54 eV	−7.54 eV	−3.63 eV	−3.63 eV

Fig. S6 Molecular orbitals and energy levels calculated in B3LYP/6-31+G(d) level of HAT derivatives.

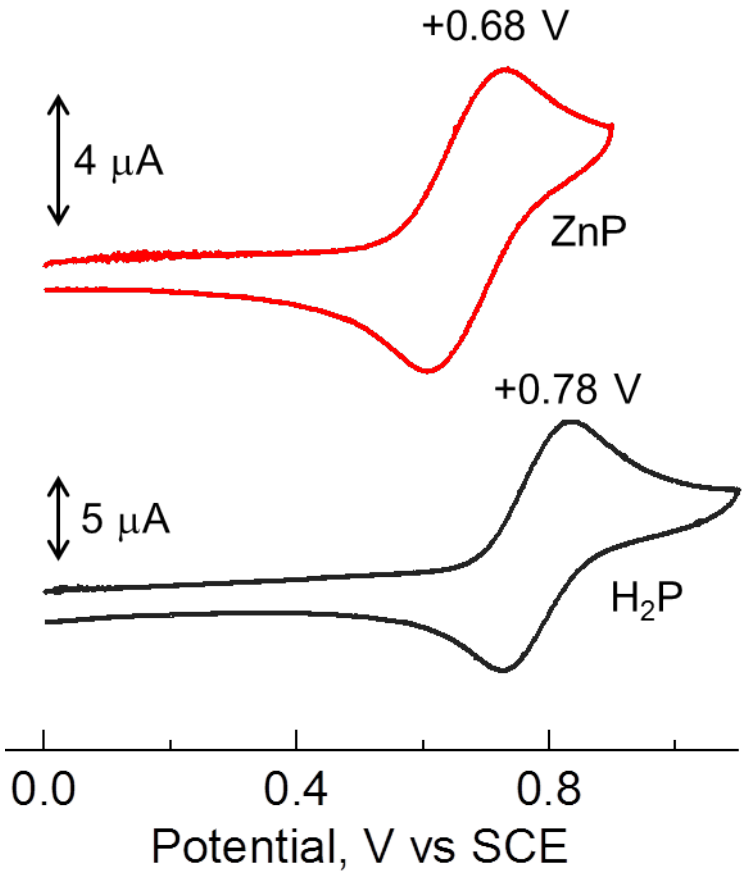


Fig. S7 Cyclic voltammograms of H_2P and ZnP in CH_2Cl_2 with 0.10 M $^nBu_4NPF_6$ as supporting electrolyte. Saturated calomel electrode (SCE) was used as a reference electrode. Scan rate: 0.1 V s^{-1}.

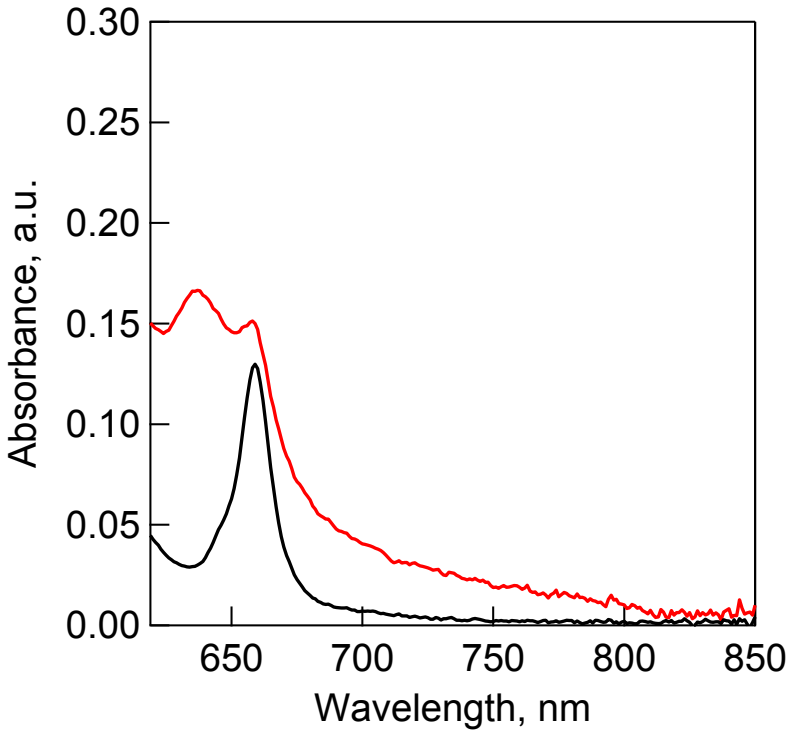


Fig. S8 CT absorption band of H_2P–C_3HAT-TIm (red) and absorption spectrum of H_2P pristine monomer (black) in CH_2Cl_2.

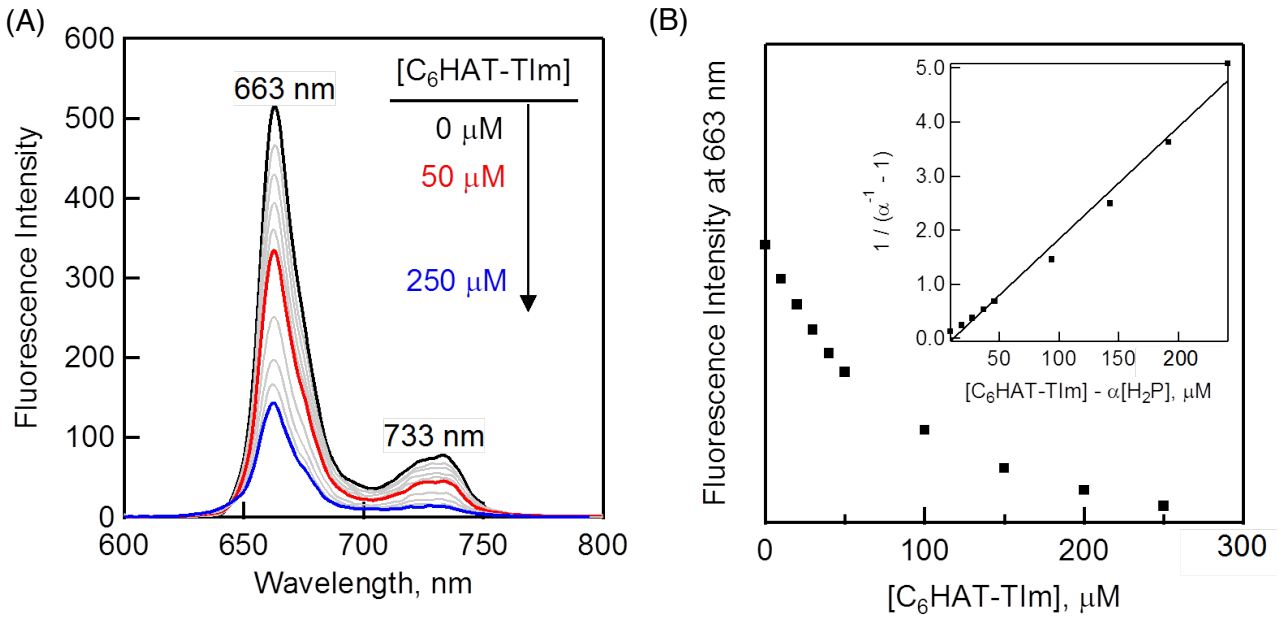


Fig. S9 (A) Fluorescence spectral changes of H_2P ([H_2P] = 10 μM) upon addition of increasing equivalents of C_6HAT-TIm (0 μM - 250 μM) in CH_2Cl_2. Excitation wavelength: 550 nm. (B) Plot of the fluorescence intensity vs [C_6HAT-TIm] at 663 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs [C_6HAT-TIm] – $\alpha[H_2P]_0$.

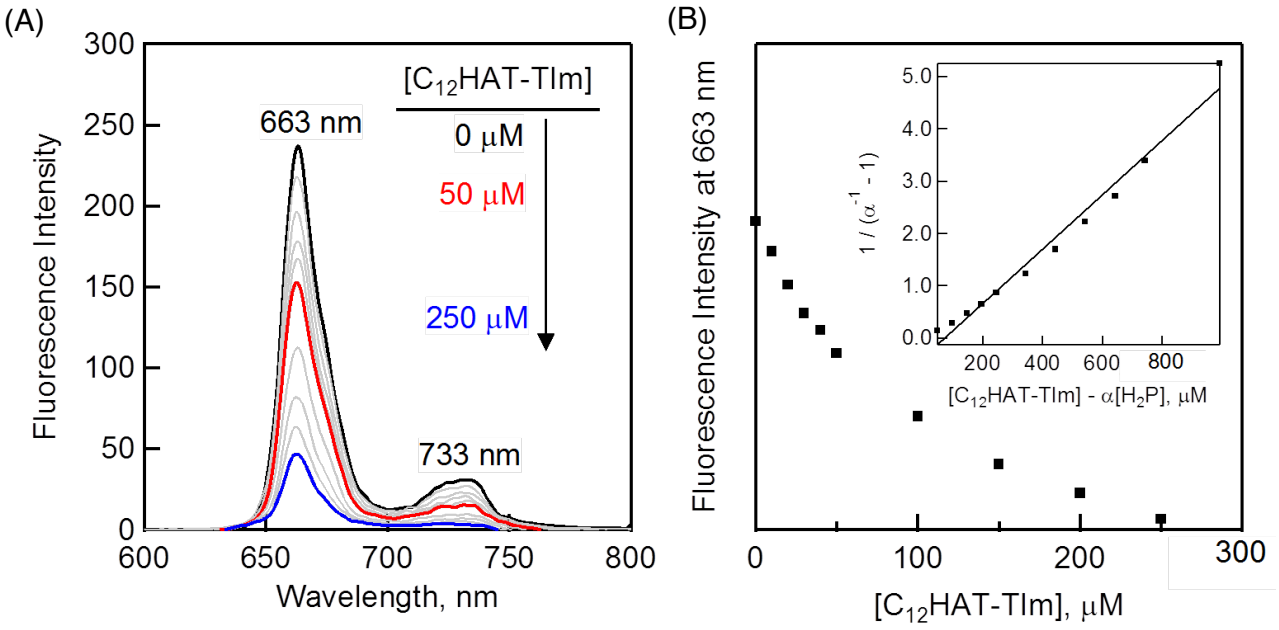


Fig. S10 (A) Fluorescence spectral changes of H_2P ([H_2P] = 10 μM) upon addition of increasing equivalents of C_6HAT-TIm (0 μM - 250 μM) in CH_2Cl_2. Excitation wavelength: 550 nm. (B) Plot of the fluorescence intensity vs [C_{12}HAT-TIm] at 663 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs [C_{12}HAT-TIm] – $\alpha[H_2P]_0$.

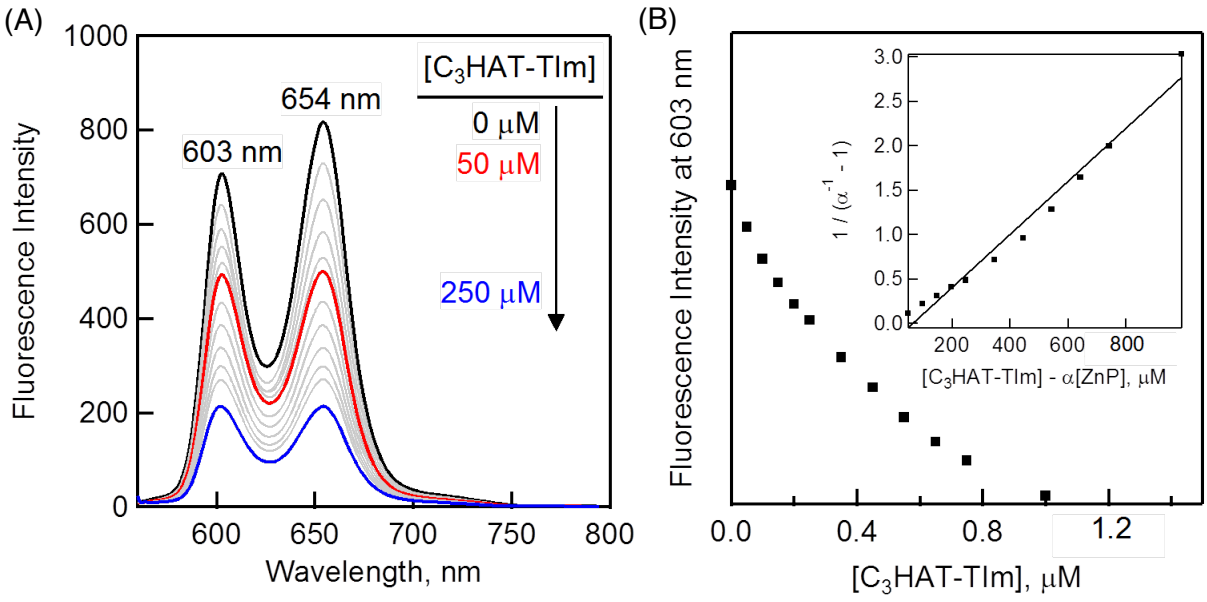


Fig. S11 (A) Fluorescence spectral changes of ZnP ([ZnP] = 10 μM) upon addition of increasing equivalents of C_3HAT-TIm (0 μM - 250 μM) in CH_2Cl_2. Excitation wavelength: 550 nm. (B) Plot of the fluorescence intensity vs [C_3HAT-TIm] at 603 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs [C_3HAT-TIm] – $\alpha[H_2P]_0$.

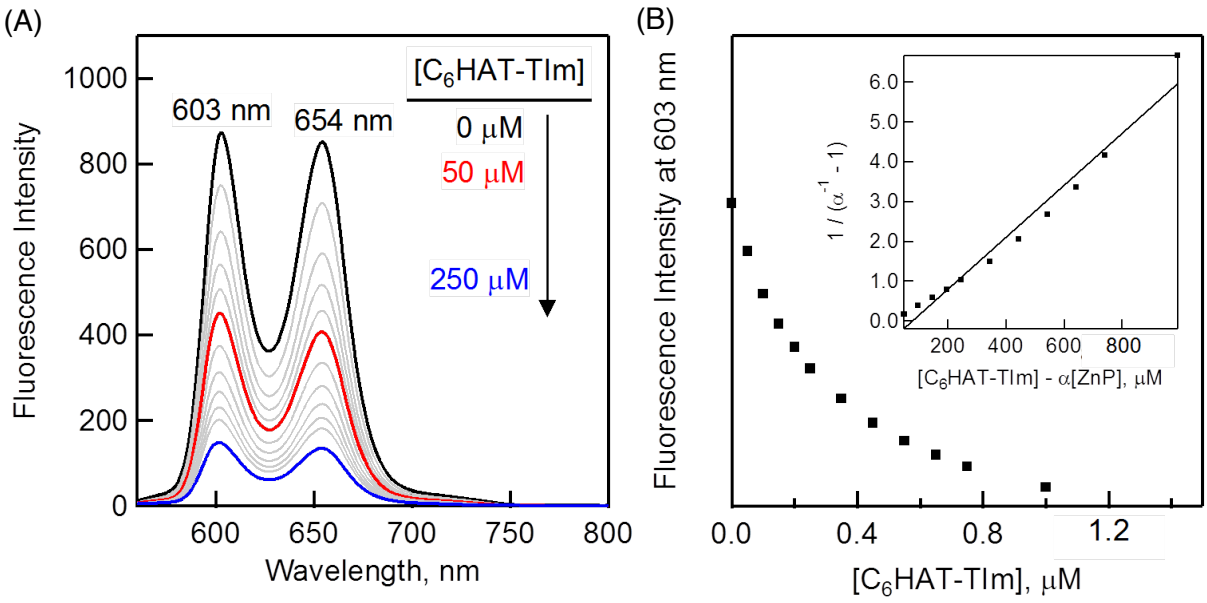


Fig. S12 (A) Fluorescence spectral changes of ZnP ([ZnP] = 10 μM) upon addition of increasing equivalents of C_6HAT-TIm (0 μM - 250 μM) in CH_2Cl_2. Excitation wavelength: 550 nm. (B) Plot of the fluorescence intensity vs [C_6HAT-TIm] at 603 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs [C_6HAT-TIm] – $\alpha[H_2P]_0$.

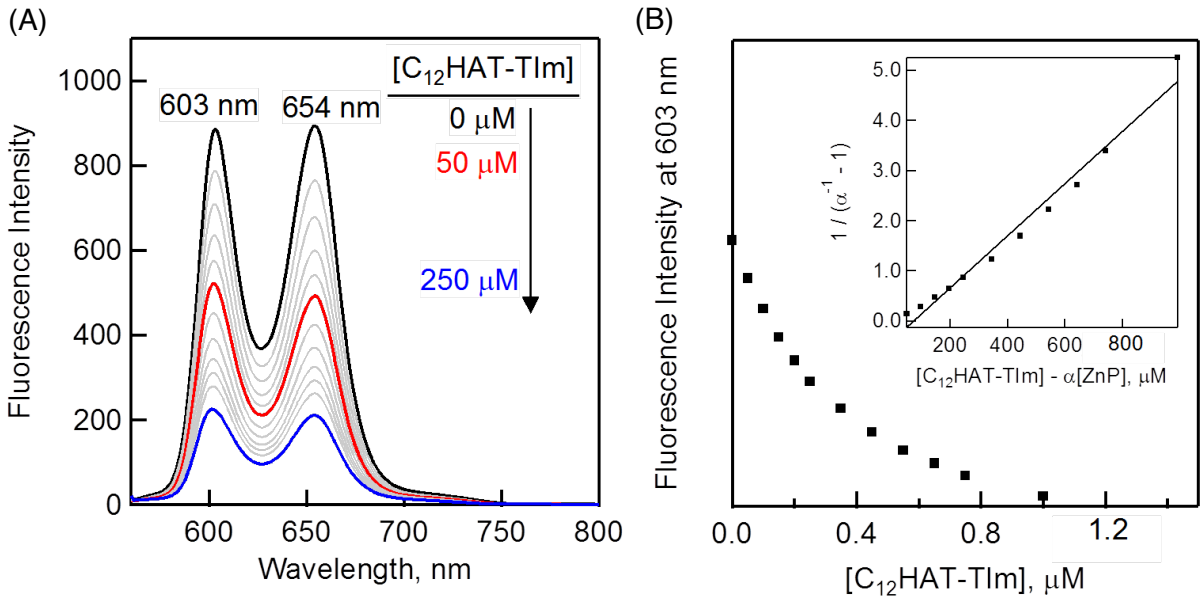


Fig. S13 (A) Fluorescence spectral changes of ZnP ([ZnP] = 10 μM) upon addition of increasing equivalents of C_{12}HAT-TIm (0 μM - 250 μM) in CH_2Cl_2. Excitation wavelength: 550 nm. (B) Plot of the fluorescence intensity vs [C_{12}HAT-TIm] at 603 nm. Inset: Plot of $(\alpha^{-1} - 1)^{-1}$ vs [C_{12}HAT-TIm] – α[H_2P]$_0$.

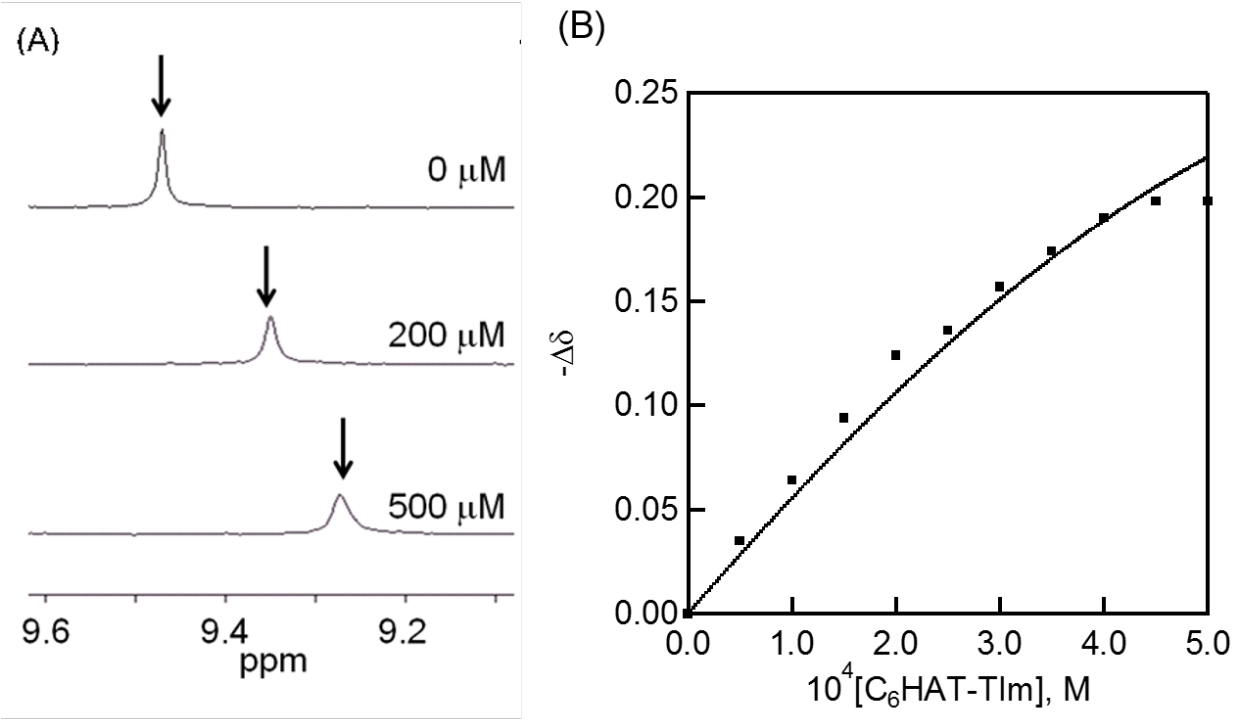


Fig. S14 (A) ^{1}H NMR titration of H_2P ([H_2P] = 500 μM) and C_6HAT-TIm upon addition of increasing equivalents of C_6HAT-TIm (0 μM - 500 μM) in $CDCl_3$. (B) ^{1}H NMR titration curve obtained from the chemical shift changes of *β* proton of H_2P by adding C_6HAT-Tim.

S15. Excitation energies and oscillator strengths for ZnP–C_3HAT-TIm by TD-DFT B3LYP/6-31G(d)//B3LYP/6-31G(d) with assignment of electronic absorption

```
Excited State   1:      Singlet-A     1.2087 eV 1025.73 nm  f=0.0000  <S**2>=0.000
    290 -> 291       0.70582     ZnP --> HAT

 Excited State   2:     Singlet-A     1.2220 eV 1014.57 nm  f=0.0070  <S**2>=0.000
    290 -> 292       0.70506     ZnP --> HAT

 Excited State   3:     Singlet-A     1.4256 eV  869.72 nm  f=0.0038  <S**2>=0.000
    289 -> 291       0.11556
    290 -> 293       0.69643     ZnP --> HAT

 Excited State   4:     Singlet-A     1.4876 eV  833.47 nm  f=0.0008  <S**2>=0.000
    289 -> 292       0.70402     ZnP --> HAT
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   5:     Singlet-A     1.5196 eV  815.89 nm  f=0.0172  <S**2>=0.000
    289 -> 291       0.69517     ZnP --> HAT
    290 -> 293      -0.11658

 Excited State   6:     Singlet-A     1.7050 eV  727.18 nm  f=0.0002  <S**2>=0.000
    289 -> 293       0.70350      ZnP --> HAT

 Excited State   7:     Singlet-A     2.1728 eV  570.63 nm  f=0.0114  <S**2>=0.000
    289 -> 295      -0.17689      ZnP --> ZnP
    290 -> 294       0.68044      ZnP --> HAT

 Excited State   8:     Singlet-A     2.2710 eV  545.94 nm  f=0.0106  <S**2>=0.000
    289 -> 294       0.29089
    289 -> 296       0.31652
    290 -> 295       0.55438      ZnP --> ZnP

 Excited State   9:     Singlet-A     2.3003 eV  538.99 nm  f=0.0047  <S**2>=0.000
    289 -> 295      -0.37929
    290 -> 294      -0.10013
    290 -> 296       0.58247      ZnP --> ZnP

 Excited State  10:     Singlet-A     2.4662 eV  502.74 nm  f=0.0047  <S**2>=0.000
    289 -> 294      -0.45103
    289 -> 296       0.10916
    290 -> 295       0.15600
    290 -> 297       0.50163      ZnP --> HAT

 Excited State  11:     Singlet-A     2.4941 eV  497.11 nm  f=0.0036  <S**2>=0.000
    289 -> 295      -0.15503
    290 -> 296      -0.13928
    290 -> 298       0.67293      ZnP --> HAT

 Excited State  12:     Singlet-A     2.4986 eV  496.21 nm  f=0.0080  <S**2>=0.000
    289 -> 294       0.41783      ZnP --> HAT
    289 -> 296      -0.29828
    290 -> 297       0.47019      ZnP --> HAT

 Excited State  13:     Singlet-A     2.5569 eV  484.89 nm  f=0.0000  <S**2>=0.000
    288 -> 292       0.69970      ZnP --> HAT

 Excited State  14:     Singlet-A     2.5715 eV  482.15 nm  f=0.0000  <S**2>=0.000
    288 -> 291       0.70520      ZnP --> HAT

 Excited State  15:     Singlet-A     2.7435 eV  451.91 nm  f=0.0171  <S**2>=0.000
    286 -> 292      -0.11116
```

```
    287 -> 291       0.16230
    289 -> 295       0.21014
    289 -> 297       0.62573      ZnP --> HAT

Excited State  16:     Singlet-A     2.7523 eV  450.48 nm  f=0.0032  <S**2>=0.000
    287 -> 292      -0.23497
    289 -> 296      -0.27880
    289 -> 298       0.58305      ZnP --> HAT

Excited State  17:     Singlet-A     2.7730 eV  447.12 nm  f=0.0000  <S**2>=0.000
    288 -> 293       0.69761      ZnP --> HAT

Excited State  18:     Singlet-A     2.7941 eV  443.73 nm  f=0.0002  <S**2>=0.000
    285 -> 291      -0.46791      ZnP --> HAT
    286 -> 292       0.15087
    287 -> 291       0.47694
    289 -> 297      -0.14989      ZnP --> HAT

Excited State  19:     Singlet-A     2.8010 eV  442.64 nm  f=0.0024  <S**2>=0.000
    285 -> 292      -0.22802
    287 -> 292       0.60539      ZnP --> HAT
    289 -> 298       0.25180

Excited State  20:     Singlet-A     2.8105 eV  441.15 nm  f=0.0000  <S**2>=0.000
    285 -> 291      -0.13790
    286 -> 292       0.60997      ZnP --> HAT
    287 -> 291      -0.27502
    289 -> 297       0.14621

Excited State  21:     Singlet-A     2.8173 eV  440.09 nm  f=0.0015  <S**2>=0.000
    285 -> 292       0.47936      ZnP --> HAT
    286 -> 291      -0.47514      ZnP --> HAT
    287 -> 292       0.16990

Excited State  22:     Singlet-A     2.8400 eV  436.56 nm  f=0.0002  <S**2>=0.000
    285 -> 291       0.48748      ZnP --> HAT
    286 -> 292       0.27234
    286 -> 293      -0.15802
    287 -> 291       0.39745

Excited State  23:     Singlet-A     2.8468 eV  435.52 nm  f=0.0010  <S**2>=0.000
    285 -> 292       0.43873      ZnP --> HAT
    286 -> 291       0.49951      ZnP --> HAT
    287 -> 292       0.16904
    287 -> 293      -0.12965

Excited State  24:     Singlet-A     2.9845 eV  415.42 nm  f=0.0001  <S**2>=0.000
    279 -> 294      -0.10487
    281 -> 292      -0.18692
    282 -> 291       0.28232
    283 -> 292       0.57617      HAT --> HAT

Excited State  25:     Singlet-A     2.9945 eV  414.04 nm  f=0.0013  <S**2>=0.000
    280 -> 292      -0.11109
    281 -> 291      -0.14556
    282 -> 292       0.38512      HAT --> HAT
    282 -> 293       0.21983
    283 -> 291       0.45813      HAT --> HAT
    283 -> 294      -0.10921
    284 -> 292       0.10673

Excited State  26:     Singlet-A     3.0058 eV  412.49 nm  f=0.0024  <S**2>=0.000
    280 -> 291      -0.14655
    282 -> 291       0.50897      ZnP --> HAT
    283 -> 292      -0.21806
```

```
    283 -> 293       0.27901
    284 -> 291       0.14694
    286 -> 293      -0.14255

Excited State  27:     Singlet-A     3.0113 eV  411.73 nm  f=0.0057  <S**2>=0.000
    285 -> 293      -0.36314
    287 -> 293       0.57582      ZnP --> HAT

Excited State  28:     Singlet-A     3.0449 eV  407.18 nm  f=0.0015  <S**2>=0.000
    282 -> 291       0.13523
    286 -> 292       0.10157
    286 -> 293       0.65532      ZnP --> HAT

Excited State  29:     Singlet-A     3.0534 eV  406.06 nm  f=0.0041  <S**2>=0.000
    283 -> 291       0.15316
    285 -> 293       0.54254      ZnP --> HAT
    286 -> 291       0.11127
    287 -> 293       0.36343

Excited State  30:     Singlet-A     3.0749 eV  403.22 nm  f=0.0037  <S**2>=0.000
    279 -> 293      -0.24141
    280 -> 292      -0.14433
    281 -> 291       0.11940
    282 -> 292       0.44118      HAT --> HAT
    283 -> 291      -0.35714
    285 -> 293       0.20571
SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 LETran=    550.
```

S16. Excitation energies and oscillator strengths for ZnP by TD-DFT B3LYP/6-31G(d)//B3LYP/6-31G(d)

```
Excited State   1:      Singlet-A     2.2874 eV  542.04 nm  f=0.0113  <S**2>=0.000
    142 ->144       -0.30484
    142 ->145        0.32326
    143 ->144        0.39839
    143 ->145        0.37567

Excited State   2:      Singlet-A     2.2874 eV  542.04 nm  f=0.0113  <S**2>=0.000
    142 ->144       -0.32326
    142 ->145       -0.30484
    143 ->144       -0.37567
    143 ->145        0.39839

Excited State   3:      Singlet-A     3.2568 eV  380.69 nm  f=0.1258  <S**2>=0.000
    141 ->144        0.65560
    142 ->144        0.20070
    143 ->145        0.16202

Excited State   4:      Singlet-A     3.2568 eV  380.69 nm  f=0.1258  <S**2>=0.000
    141 ->145        0.65560
    142 ->145        0.20070
    143 ->144       -0.16202
This state for optimization and/or second-order correction.
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State   5:      Singlet-A     3.3077 eV  374.84 nm  f=0.8884  <S**2>=0.000
    141 ->144       -0.25900
    142 ->144        0.50808
    143 ->145        0.40917
    143 <-145       -0.10285

Excited State   6:      Singlet-A     3.3077 eV  374.84 nm  f=0.8884  <S**2>=0.000
    141 ->145       -0.25900
    142 ->145        0.50808
    143 ->144       -0.40917
    143 <-144        0.10285

Excited State   7:      Singlet-A     3.6571 eV  339.03 nm  f=0.0000  <S**2>=0.000
    139 ->144        0.48271
    139 ->145        0.11556
    140 ->144       -0.11556
    140 ->145        0.48271

Excited State   8:      Singlet-A     3.7173 eV  333.53 nm  f=0.0001  <S**2>=0.000
    139 ->144        0.46944
    139 ->145       -0.15799
    140 ->144       -0.15799
    140 ->145       -0.46943

Excited State   9:      Singlet-A     3.7947 eV  326.73 nm  f=0.0000  <S**2>=0.000
    143 ->146        0.68753

Excited State  10:      Singlet-A     3.7965 eV  326.57 nm  f=0.0384  <S**2>=0.000
    138 ->144        0.65518
    138 ->145       -0.23124

Excited State  11:      Singlet-A     3.7965 eV  326.57 nm  f=0.0384  <S**2>=0.000
    138 ->144        0.23124
    138 ->145        0.65518

Excited State  12:      Singlet-A     3.8374 eV  323.09 nm  f=0.0000  <S**2>=0.000
    139 ->144        0.15690
```

```
   139 ->145        0.46622
   140 ->144        0.46623
   140 ->145       -0.15689

Excited State  13:     Singlet-A     3.9156 eV  316.64 nm  f=0.0000  <S**2>=0.000
   139 ->144       -0.11593
   139 ->145        0.48427
   140 ->144       -0.48426
   140 ->145       -0.11593

Excited State  14:     Singlet-A     4.0792 eV  303.94 nm  f=0.0000  <S**2>=0.000
   135 ->145       -0.10175
   136 ->144        0.10175
   142 ->146        0.67294

Excited State  15:     Singlet-A     4.2851 eV  289.34 nm  f=0.1464  <S**2>=0.000
   137 ->144        0.69172

Excited State  16:     Singlet-A     4.2851 eV  289.34 nm  f=0.1464  <S**2>=0.000
   137 ->145        0.69172

Excited State  17:     Singlet-A     4.4227 eV  280.34 nm  f=0.0000  <S**2>=0.000
   135 ->144       -0.36211
   135 ->145        0.34040
   136 ->144        0.34040
   136 ->145        0.36211

Excited State  18:     Singlet-A     4.5347 eV  273.41 nm  f=0.0000  <S**2>=0.000
   135 ->144        0.34012
   135 ->145        0.36181
   136 ->144        0.36182
   136 ->145       -0.34012

Excited State  19:     Singlet-A     4.7782 eV  259.48 nm  f=0.0000  <S**2>=0.000
   135 ->144       -0.22842
   135 ->145        0.29128
   136 ->144       -0.29128
   136 ->145       -0.22842
   141 ->146        0.42452
   142 ->146        0.12699
   143 ->149       -0.10595

Excited State  20:     Singlet-A     4.7851 eV  259.10 nm  f=0.0000  <S**2>=0.000
   135 ->144        0.17853
   135 ->145       -0.22728
   136 ->144        0.22728
   136 ->145        0.17852
   141 ->146        0.53916
   142 ->146       -0.10443

Excited State  21:     Singlet-A     4.9276 eV  251.61 nm  f=0.0000  <S**2>=0.000
   135 ->144        0.36989
   135 ->145        0.29020
   136 ->144       -0.29020
   136 ->145        0.36989
   142 ->149        0.13726
   143 ->146        0.12807

Excited State  22:     Singlet-A     5.0929 eV  243.45 nm  f=0.0000  <S**2>=0.000
   143 ->147        0.70417

Excited State  23:     Singlet-A     5.2764 eV  234.98 nm  f=0.0701  <S**2>=0.000
   140 ->146        0.69995

Excited State  24:     Singlet-A     5.2764 eV  234.98 nm  f=0.0701  <S**2>=0.000
```

```
   139 ->146        0.69995

Excited State  25:     Singlet-A     5.2958 eV  234.12 nm  f=0.0000  <S**2>=0.000
   138 ->146        0.69864

Excited State  26:     Singlet-A     5.3317 eV  232.54 nm  f=0.0000  <S**2>=0.000
   142 ->147        0.70157

Excited State  27:     Singlet-A     5.3451 eV  231.96 nm  f=0.0070  <S**2>=0.000
   143 ->148        0.70431

Excited State  28:     Singlet-A     5.4105 eV  229.16 nm  f=0.0478  <S**2>=0.000
   134 ->144        0.66890
   134 ->145       -0.19954

Excited State  29:     Singlet-A     5.4105 eV  229.16 nm  f=0.0478  <S**2>=0.000
   134 ->144        0.19954
   134 ->145        0.66890

Excited State  30:     Singlet-A     5.5684 eV  222.65 nm  f=0.0000  <S**2>=0.000
   132 ->144       -0.48765
   133 ->145        0.48777
SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 LETran=    550.
```

S17. Excitation energies and oscillator strengths for C_3HAT-TIm by TD-DFT B3LYP/6-31G(d)//B3LYP/6-31G(d)

```
Excited State   1:      Singlet-A     2.9667 eV  417.92 nm  f=0.0000  <S**2>=0.000
    146 ->148        0.48047
    147 ->149        0.48875

 Excited State   2:      Singlet-A     2.9739 eV  416.91 nm  f=0.0000  <S**2>=0.000
    146 ->148        0.44127
    146 ->151        0.11108
    147 ->149       -0.43132
    147 ->150        0.28949

 Excited State   3:      Singlet-A     2.9740 eV  416.89 nm  f=0.0000  <S**2>=0.000
    146 ->149        0.43512
    146 ->150        0.29013
    147 ->148        0.43712
    147 ->151       -0.11091

 Excited State   4:      Singlet-A     3.0393 eV  407.94 nm  f=0.0047  <S**2>=0.000
    143 ->150       -0.16801
    145 ->150        0.20449
    146 ->149        0.44776
    147 ->148       -0.44571
 This state for optimization and/or second-order correction.
 Copying the excited state density for this state as the 1-particle RhoCI density.

 Excited State   5:      Singlet-A     3.1325 eV  395.80 nm  f=0.0001  <S**2>=0.000
    143 ->148        0.29784
    145 ->148       -0.37550
    146 ->148       -0.12059
    146 ->151       -0.11717
    147 ->149        0.11994
    147 ->150        0.43908

 Excited State   6:      Singlet-A     3.1329 eV  395.75 nm  f=0.0000  <S**2>=0.000
    143 ->149       -0.29599
    145 ->149        0.37704
    146 ->149       -0.11974
    146 ->150        0.43900
    147 ->148       -0.11939
    147 ->151        0.11746

 Excited State   7:      Singlet-A     3.4277 eV  361.71 nm  f=0.0000  <S**2>=0.000
    140 ->148        0.44957
    140 ->152       -0.11006
    141 ->148        0.31218
    141 ->151        0.20853
    142 ->149        0.31054

 Excited State   8:      Singlet-A     3.4278 eV  361.70 nm  f=0.0000  <S**2>=0.000
    140 ->149        0.44868
    140 ->153       -0.10988
    141 ->149       -0.31218
    142 ->148        0.31308
    142 ->151       -0.20861
    145 ->148        0.10255

 Excited State   9:      Singlet-A     3.4460 eV  359.80 nm  f=0.0000  <S**2>=0.000
    140 ->151       -0.21262
    141 ->148       -0.45367
    141 ->152        0.11060
    142 ->149        0.45483
    142 ->153       -0.11114
```

```
Excited State  10:     Singlet-A     3.5022 eV  354.02 nm  f=0.0000  <S**2>=0.000
   140 ->148       -0.10212
   143 ->149        0.22457
   145 ->149       -0.41067
   146 ->149       -0.17335
   146 ->150        0.44052
   147 ->148       -0.17410

Excited State  11:     Singlet-A     3.5030 eV  353.94 nm  f=0.0001  <S**2>=0.000
   140 ->149       -0.10620
   143 ->148       -0.21949
   145 ->148        0.41480
   146 ->148       -0.16898
   147 ->149        0.16831
   147 ->150        0.44125

Excited State  12:     Singlet-A     3.5345 eV  350.79 nm  f=0.0000  <S**2>=0.000
   143 ->148       -0.42701
   144 ->149        0.48627
   145 ->148       -0.23891

Excited State  13:     Singlet-A     3.5658 eV  347.71 nm  f=0.0000  <S**2>=0.000
   137 ->148       -0.14932
   138 ->149        0.14829
   143 ->149        0.41058
   144 ->148        0.46810
   145 ->149        0.23135

Excited State  14:     Singlet-A     3.6010 eV  344.30 nm  f=0.0000  <S**2>=0.000
   140 ->150        0.36845
   141 ->149        0.40265
   142 ->148        0.40096

Excited State  15:     Singlet-A     3.6202 eV  342.47 nm  f=0.0018  <S**2>=0.000
   143 ->150       -0.37085
   145 ->150        0.50566
   146 ->149       -0.20744
   147 ->148        0.20586

Excited State  16:     Singlet-A     3.6260 eV  341.93 nm  f=0.0000  <S**2>=0.000
   140 ->148        0.38203
   141 ->148       -0.29273
   142 ->149       -0.28939
   142 ->150        0.37813

Excited State  17:     Singlet-A     3.6260 eV  341.93 nm  f=0.0000  <S**2>=0.000
   140 ->149        0.38459
   141 ->149        0.28775
   141 ->150        0.37866
   142 ->148       -0.29154

Excited State  18:     Singlet-A     3.7769 eV  328.27 nm  f=0.0950  <S**2>=0.000
   139 ->149        0.15222
   143 ->149       -0.36477
   144 ->148        0.46396
   145 ->149       -0.28886

Excited State  19:     Singlet-A     3.7771 eV  328.25 nm  f=0.0940  <S**2>=0.000
   139 ->148        0.15014
   143 ->148        0.37043
   144 ->149        0.46272
   145 ->148        0.28193

Excited State  20:     Singlet-A     3.8638 eV  320.89 nm  f=0.2075  <S**2>=0.000
```

```
   144 ->150        0.67738

Excited State  21:     Singlet-A     3.8645 eV  320.83 nm  f=0.2078  <S**2>=0.000
   143 ->150        0.54030
   145 ->150        0.40990

Excited State  22:     Singlet-A     3.9396 eV  314.72 nm  f=0.0823  <S**2>=0.000
   138 ->150       -0.11816
   139 ->149        0.66977

Excited State  23:     Singlet-A     3.9398 eV  314.70 nm  f=0.0819  <S**2>=0.000
   137 ->150        0.11801
   139 ->148        0.67126

Excited State  24:     Singlet-A     3.9863 eV  311.02 nm  f=0.0001  <S**2>=0.000
   140 ->148       -0.29961
   141 ->148        0.19469
   142 ->149        0.19235
   142 ->150        0.56311

Excited State  25:     Singlet-A     3.9864 eV  311.02 nm  f=0.0003  <S**2>=0.000
   140 ->149       -0.30020
   141 ->149       -0.19464
   141 ->150        0.56286
   142 ->148        0.19325

Excited State  26:     Singlet-A     3.9940 eV  310.42 nm  f=0.0000  <S**2>=0.000
   140 ->150        0.58341
   141 ->149       -0.27766
   142 ->148       -0.27831

Excited State  27:     Singlet-A     4.0657 eV  304.95 nm  f=0.0001  <S**2>=0.000
   137 ->148        0.38632
   138 ->149       -0.38682
   139 ->150        0.40455
   144 ->148        0.11720

Excited State  28:     Singlet-A     4.1354 eV  299.81 nm  f=0.0002  <S**2>=0.000
   136 ->149        0.13227
   142 ->150        0.12598
   143 ->153        0.10177
   145 ->149       -0.11405
   145 ->153       -0.13572
   146 ->153        0.18092
   147 ->151        0.55942
   147 ->152        0.18155

Excited State  29:     Singlet-A     4.1355 eV  299.80 nm  f=0.0000  <S**2>=0.000
   136 ->148        0.13362
   141 ->150       -0.12656
   143 ->152        0.10410
   145 ->148       -0.10998
   145 ->152       -0.13336
   146 ->151        0.55859
   146 ->152       -0.18263
   147 ->153        0.18145

Excited State  30:     Singlet-A     4.1786 eV  296.71 nm  f=0.0002  <S**2>=0.000
   133 ->150        0.15294
   134 ->148       -0.13284
   135 ->149       -0.13394
   143 ->151        0.21948
   145 ->151       -0.29127
   146 ->152        0.36212
   147 ->153        0.36263
```

```
SavETr:  write IOETrn=   770 NScale= 10 NData=  16 NLR=1 LETran=    550.
```

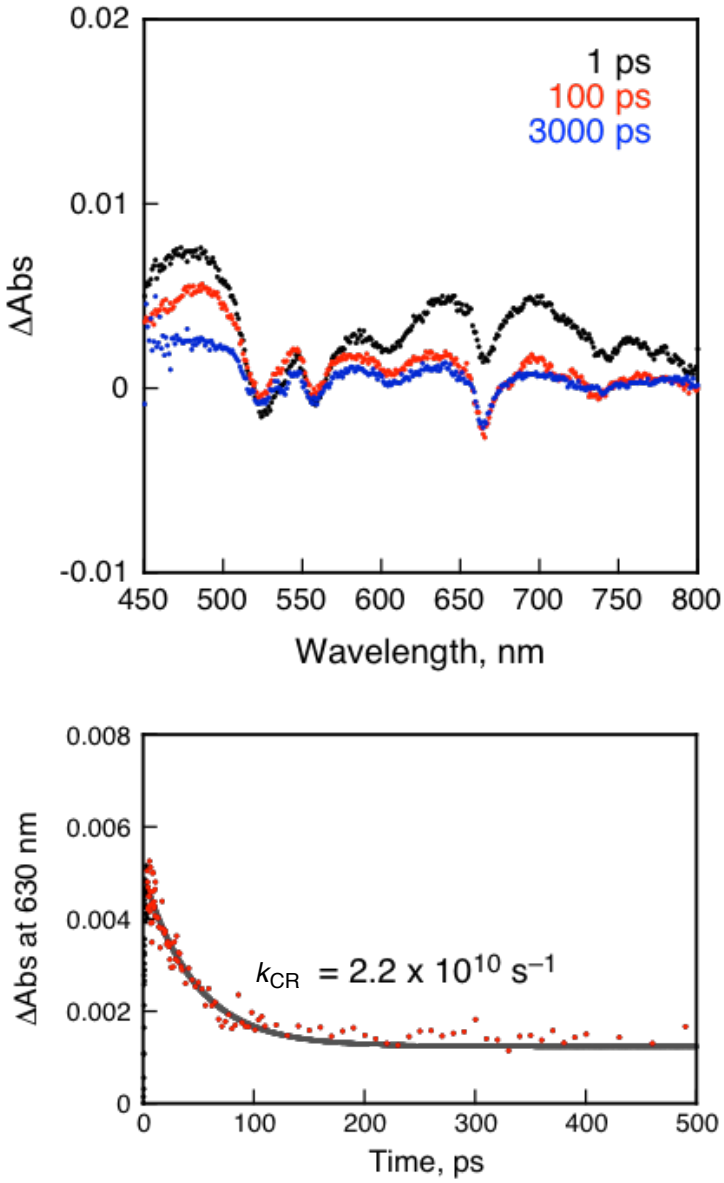


Fig. S18 Femtosecond laser-induced transient absorption spectra and corresponding time profiles of H_2P–C_6HAT-TIm recorded at 1.0 ps (black), 100 ps (red) and 3000 ps (blue) after laser excitation in toluene. The concentrations of H_2P and C_{12}HAT-TIm are 10 μM and 8.0 mM, respectively. Excitation wavelength is 430 nm.

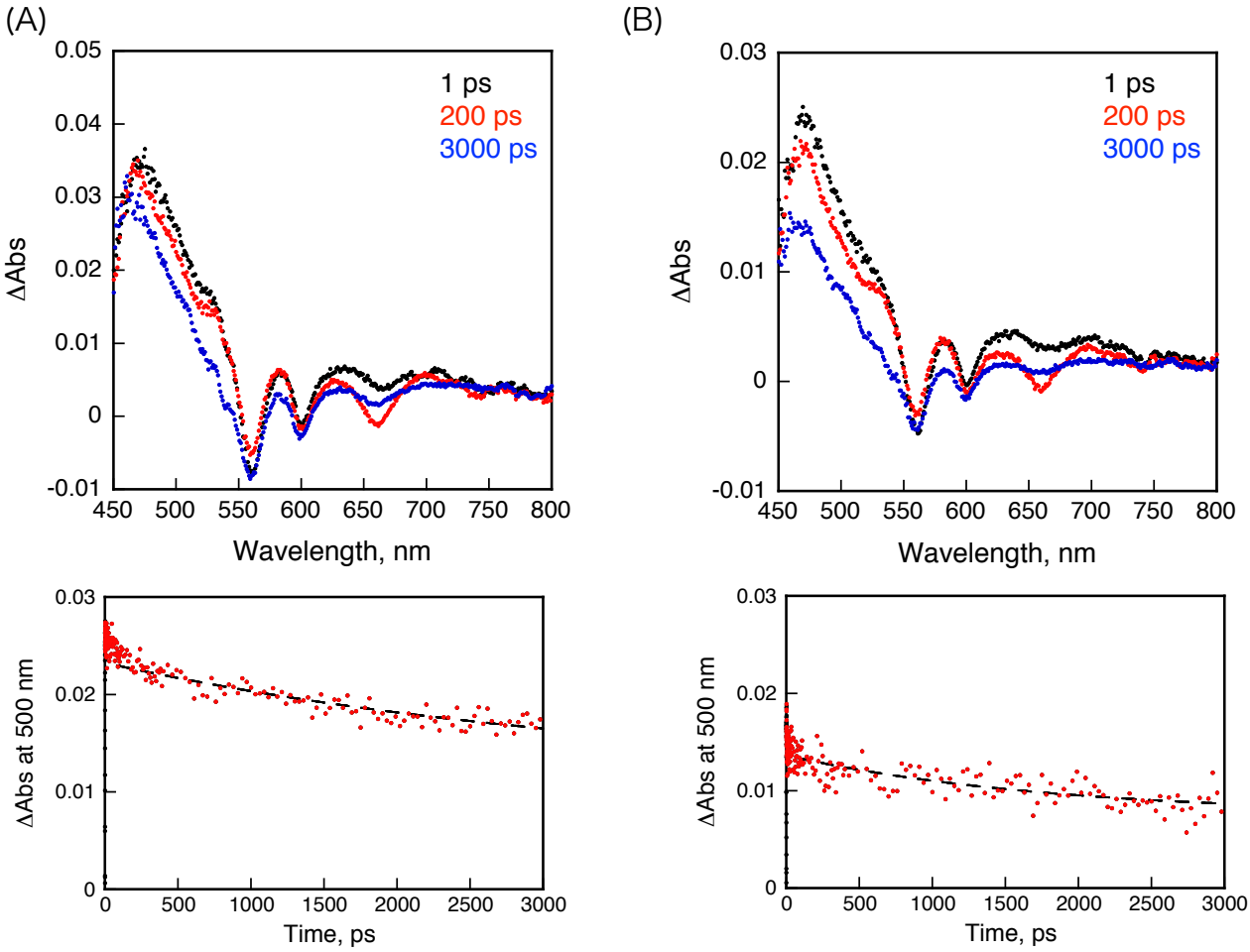


Fig. S19 Femtosecond laser-induced transient absorption spectra and corresponding time profiles of (A) ZnP and (B) ZnP–C_3HAT-TIm recorded at 1.0 ps (black), 100 ps (red) and 3000 ps (blue) after laser excitation in toluene. The concentrations of ZnP and C_3HAT-TIm are 10 μM and 8.0 mM, respectively. Excitation wavelength is 430 nm.

Table S20

Total energies of H_2P, ZnP and HAT-TIm calculated at the B3LYP/6-31G(d) level of theory and stabilization energies (E_{stab})

	Porphyrin E_D, hartree	HAT-TIm E_A, hartree	Por–HAT-TIm E_{DA}, hartree	E_{stab},[a] kcal mol^{-1}
ZnP–C_3HAT-TIm	-4497.37835886	-1985.7111643	-6483.0997842	-6.44
ZnP–C_6HAT-TIm	-4497.37835886	-2339.5348369	-6836.9235661	-6.51
ZnP–C_{12}HAT-TIm	-4497.37835886	-3047.1818926	-7544.5707800	-6.61
H_2P–C_3HAT-TIm	-2719.3439945	-1985.7111643	-4705.0659022	-6.74
H_2P–C_6HAT-TIm	-2719.3439945	-2339.5348369	-5058.8896375	-6.78
H_2P–C_{12}HAT-TIm	-2719.3439945	-3047.1818926	-5766.5368438	-6.88

[a] $E_{stab} = E_{DA} - (E_A + E_D)$.