Supporting Information

for

Synthesis and Excited-State Photodynamics of Perylene-Bis(Imide)–Oxochlorin Dyads. A Charge-Separation Motif

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Figure Descriptions

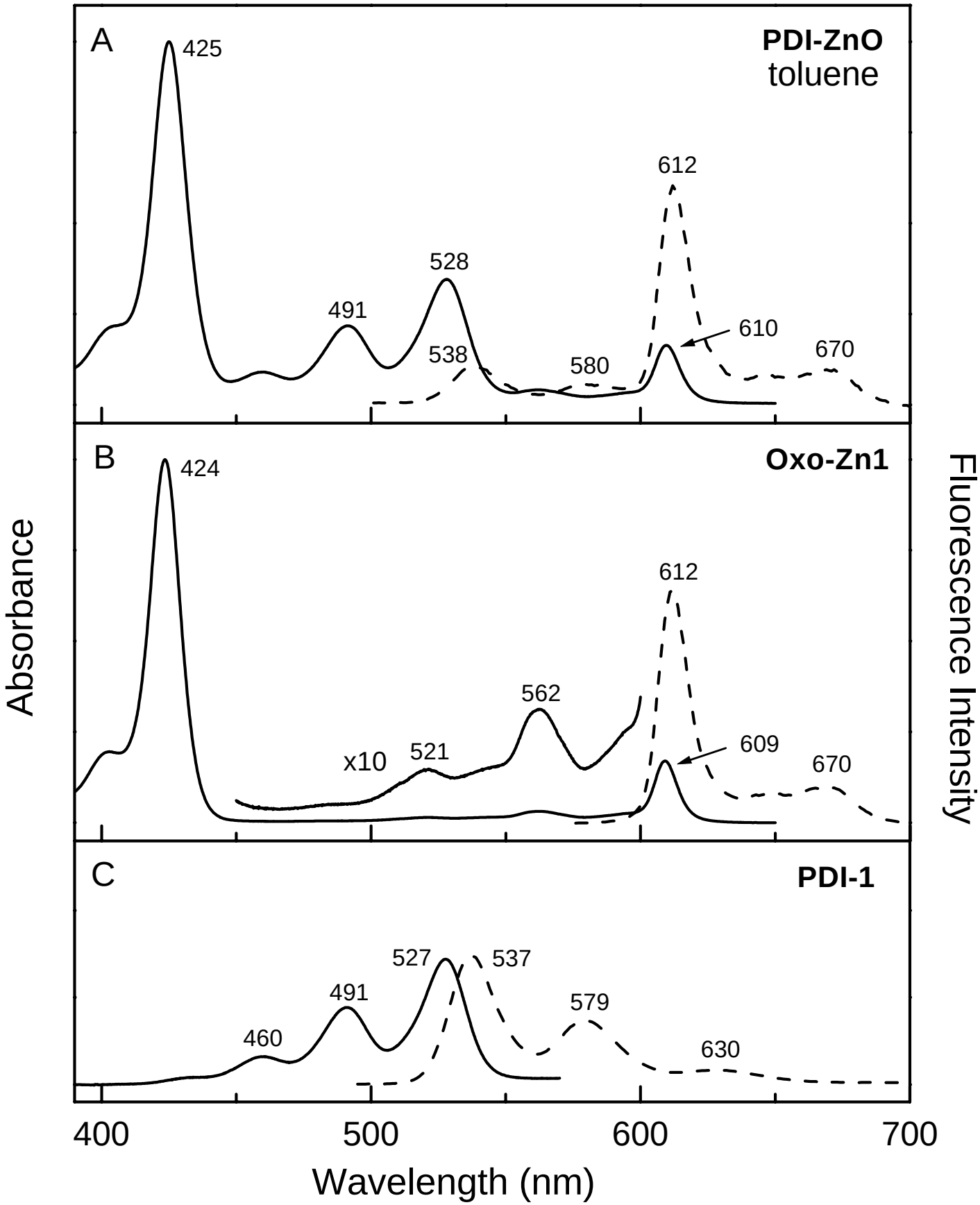
Figures SI-1 to SI-6:

Absorption spectra (solid) and emission spectra (dashed) for the dyads in toluene and benzonitrile at room temperature are shown in Figures SI-1 to SI-6. The spectrum in Figure SI-1 for **PDI-ZnO** was given in Figure 2 of the paper and is reproduced here for completeness. The emission spectra were acquired using primarily excitation of the oxochlorin at 392 nm. For each figure, the emission spectra for the dyad in A and oxochlorin monomer in B have been corrected for the absorbance at the excitation wavelength and are on the same scale (except for any indicated scale factors by which a spectrum have been multiplied). The emission intensities for the PDI monomer in each figure has been reduced by at least an order of magnitude after correction for absorbance at the excitation wavelength (480 nm).

The most notable differences among the absorption spectra are as follows. (1) The oxochlorin long-wavelength, $Q_Y(0,0)$ absorption band shifts from 610 nm for **PDI-ZnO** to 617 nm for **PDI-MgO** and to 643 nm for **PDI-FbO**; this feature has diminished intensity along this series (Zn > Mg > Fb). (2) The Soret band for the same four arrays in toluene lies at 425, 427, and 418 nm. (3) The Q_x features between 500 and 550 nm for **PDI-FbO** are stronger than for the metallooxochlorin-containing dyads, but remain overwhelmed by the perylene absorption. (4) The oxochlorin absorption bands for the metallooxochlorin-containing arrays are bathochromically shifted by 3-6 nm in benzonitrile compared to toluene, and the $Q_y(0,0)$ band has slightly diminished intensity (relative to the perylene absorption, for example); however, the oxochlorin absorption features of **PDI-FbO** are virtually the same in the two solvents, reflecting the absence of metal-solvent coordination. (5) The PDI bands blue shift by 2-4 nm between toluene and benzonitrile.

Figures SI-7 to SI-18:

Complete spectral characterization (^{1}H NMR and LD-MS) of all new compounds.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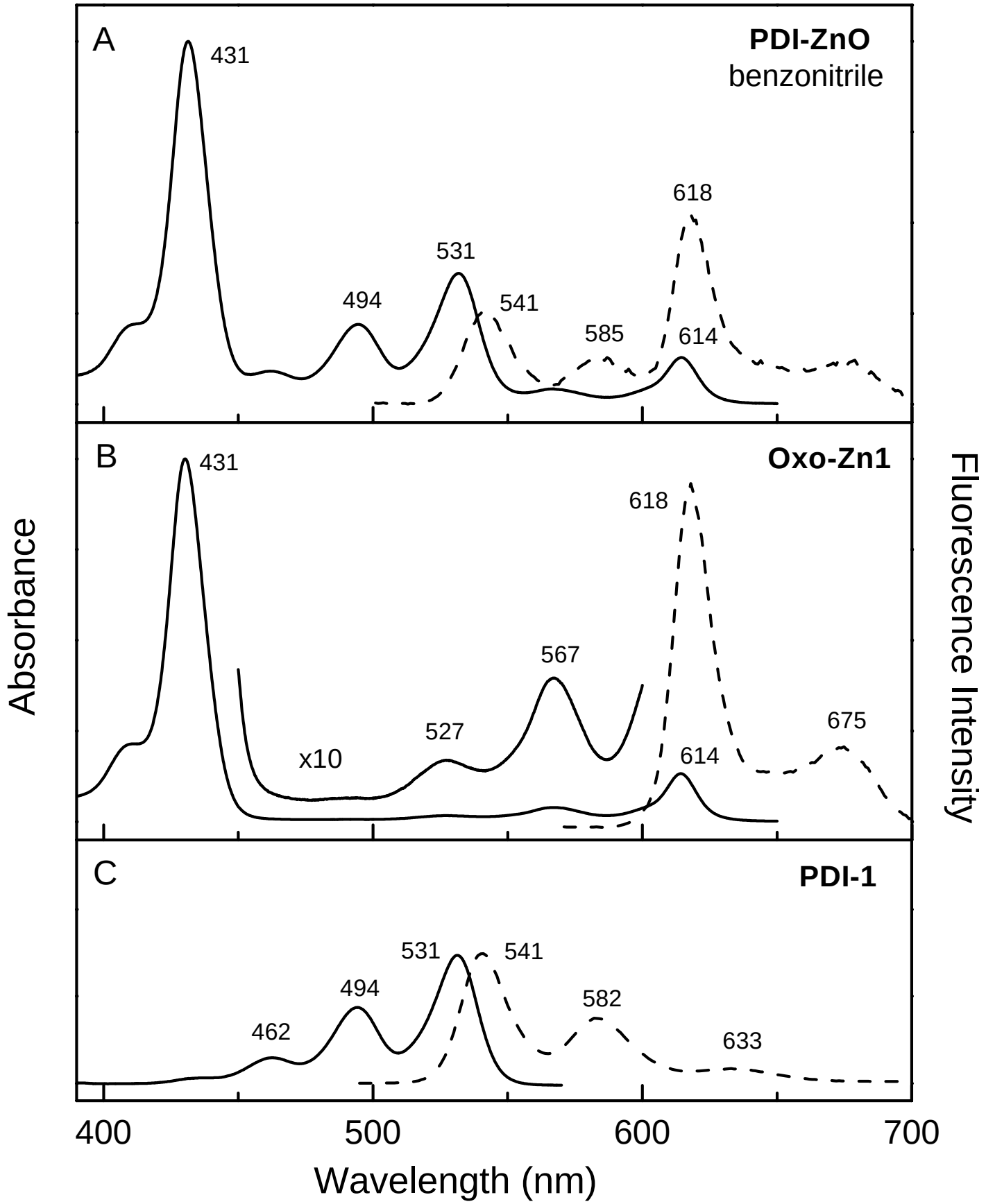
425
PDI-ZnO
toluene
612
528
491
610
538
580
670
B
424
Oxo-Zn1
612
562
x10
521
609
670
C
PDI-1
527
537
491
579
460
630
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-1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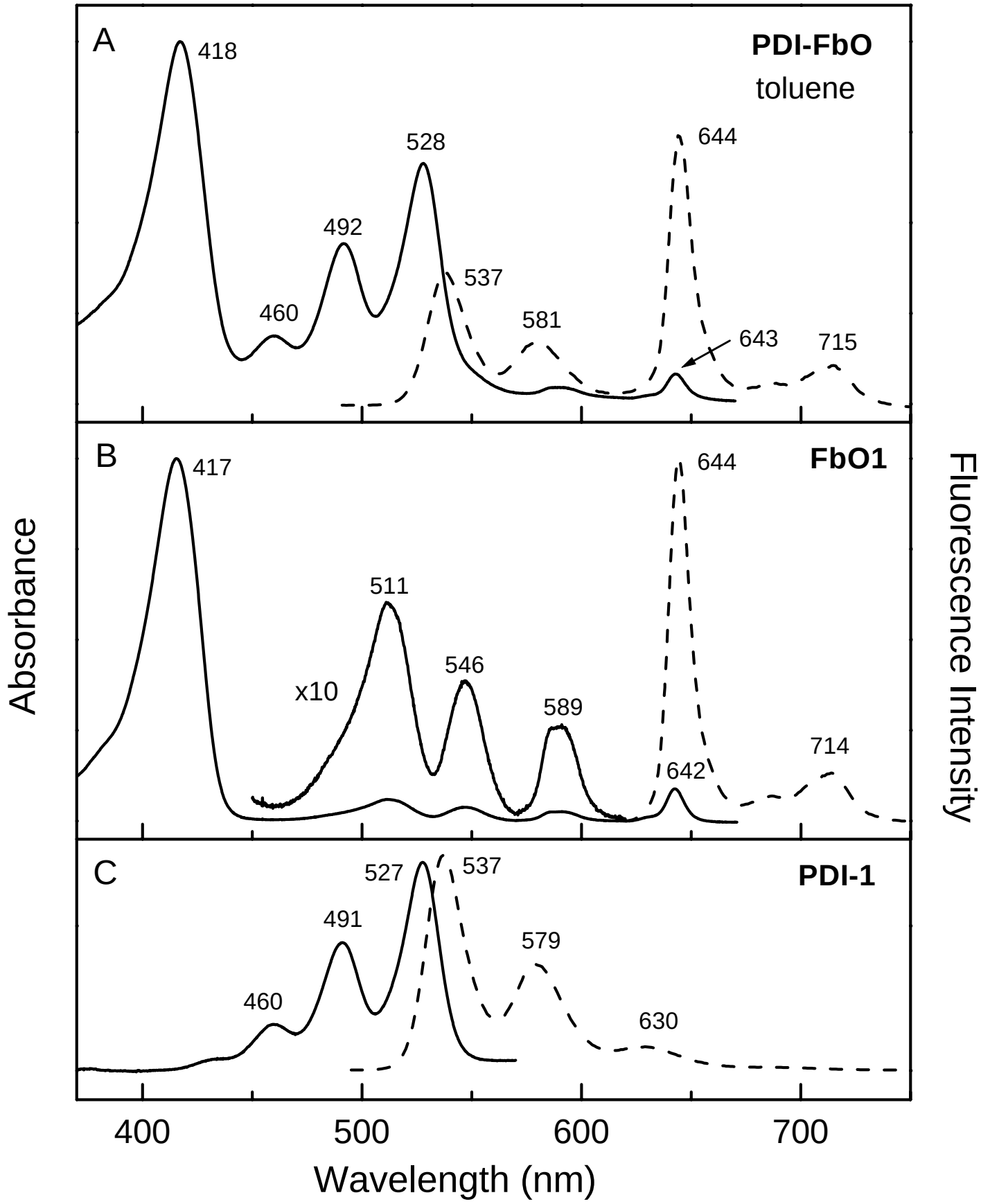
PDI-ZnO
benzonitrile
431
494
531
541
585
614
618
B
Oxo-Zn1
431
618
567
527
675
x10
614
C
PDI-1
531
541
494
582
462
633
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-2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418
PDI-FbO
toluene
528
644
492
537
460
581
643
715
B
417
644
FbO1
511
546
x10
589
714
642
C
527
537
PDI-1
491
579
460
630
400
500
600
700
Wavelength (nm)
Absorbance
Fluorescence Intensity

Figure SI-3

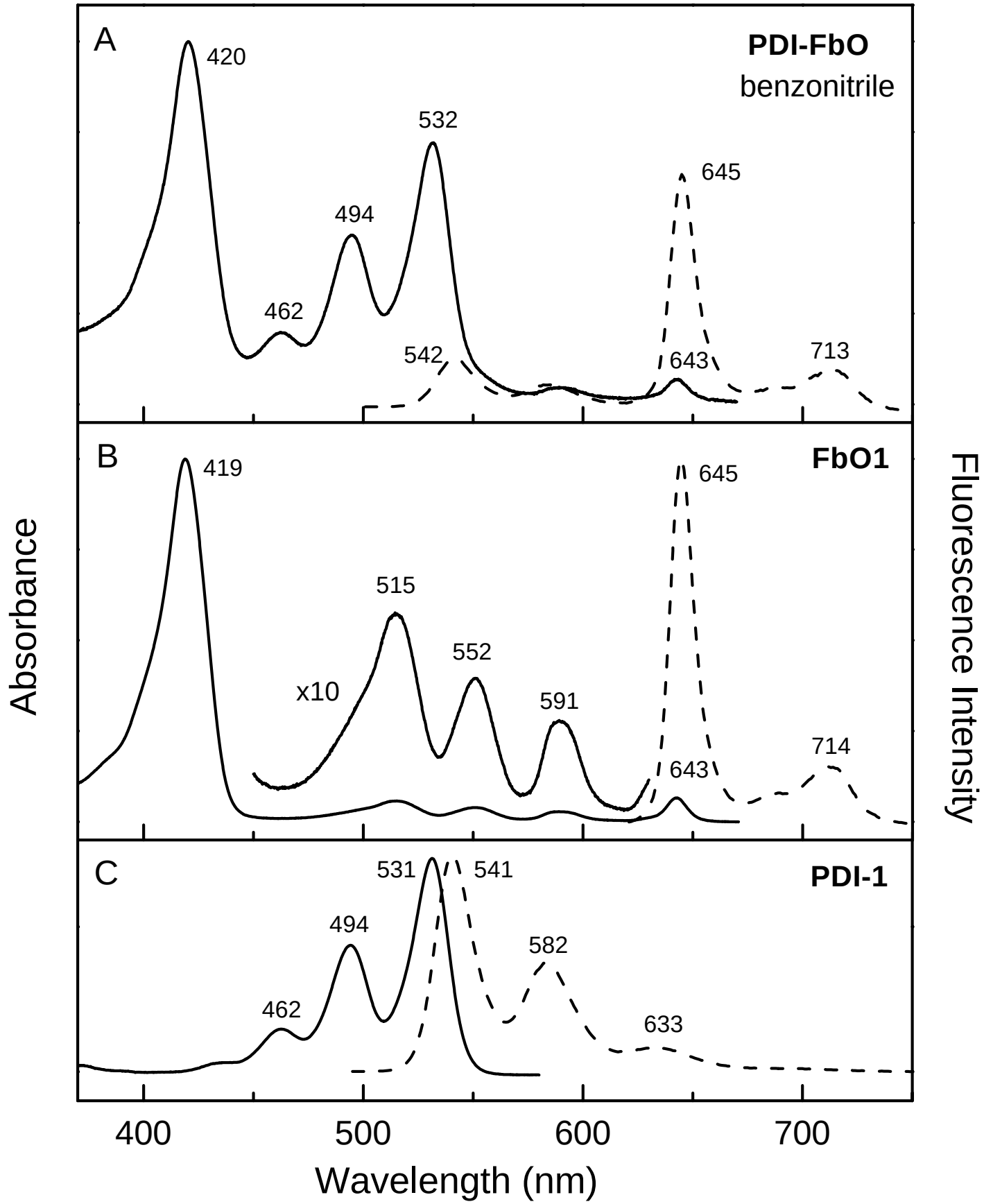

A
PDI-FbO
benzonitrile
420
532
645
494
462
542
643
713
B
FbO1
419
645
515
552
x10
591
714
643
C
PDI-1
531
541
494
582
462
633
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-4

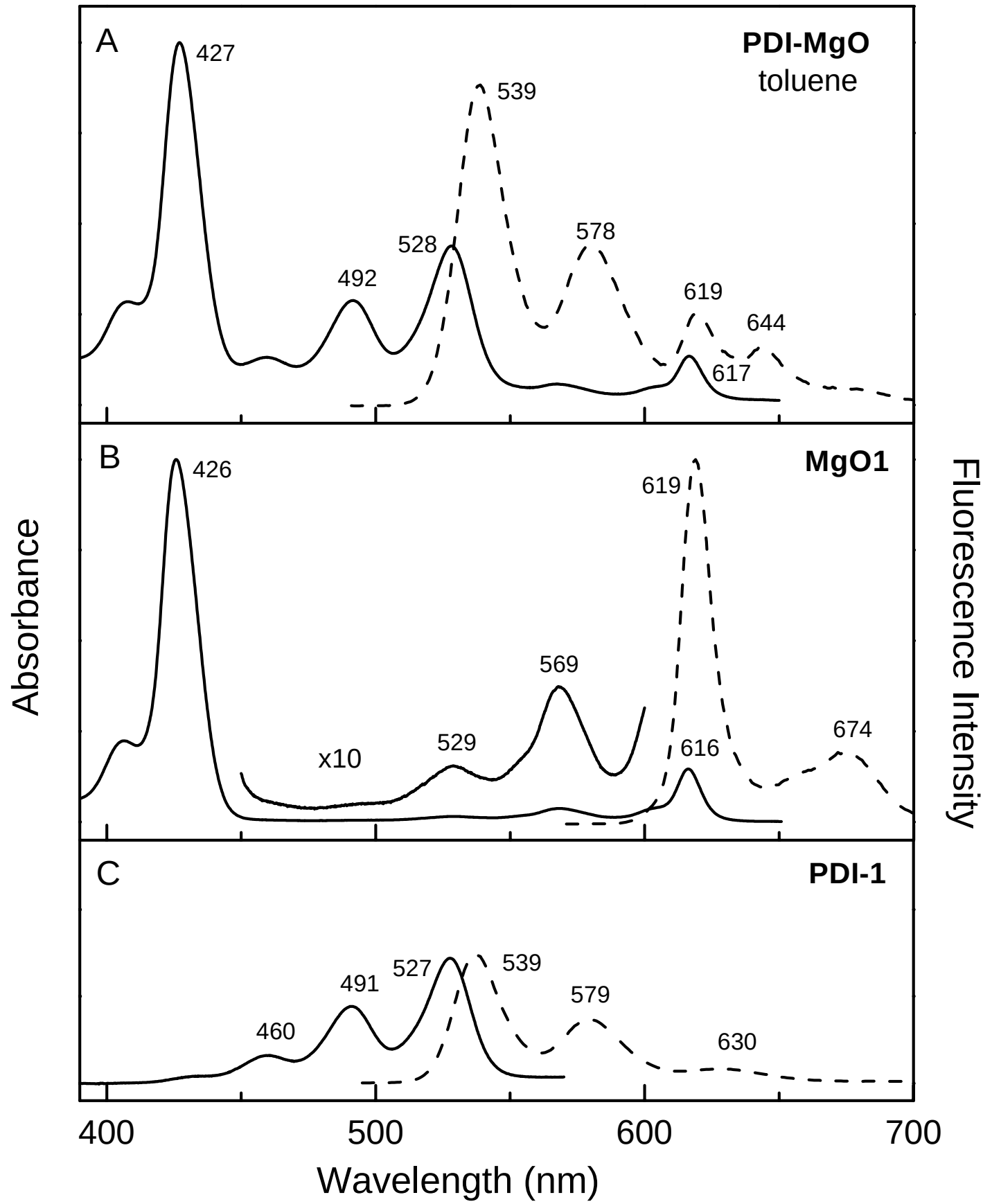

A
427
539
528
578
492
619
644
617
PDI-MgO
toluene
B
426
619
MgO1
569
529
x10
616
674
C
PDI-1
527
539
491
579
460
630
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-5

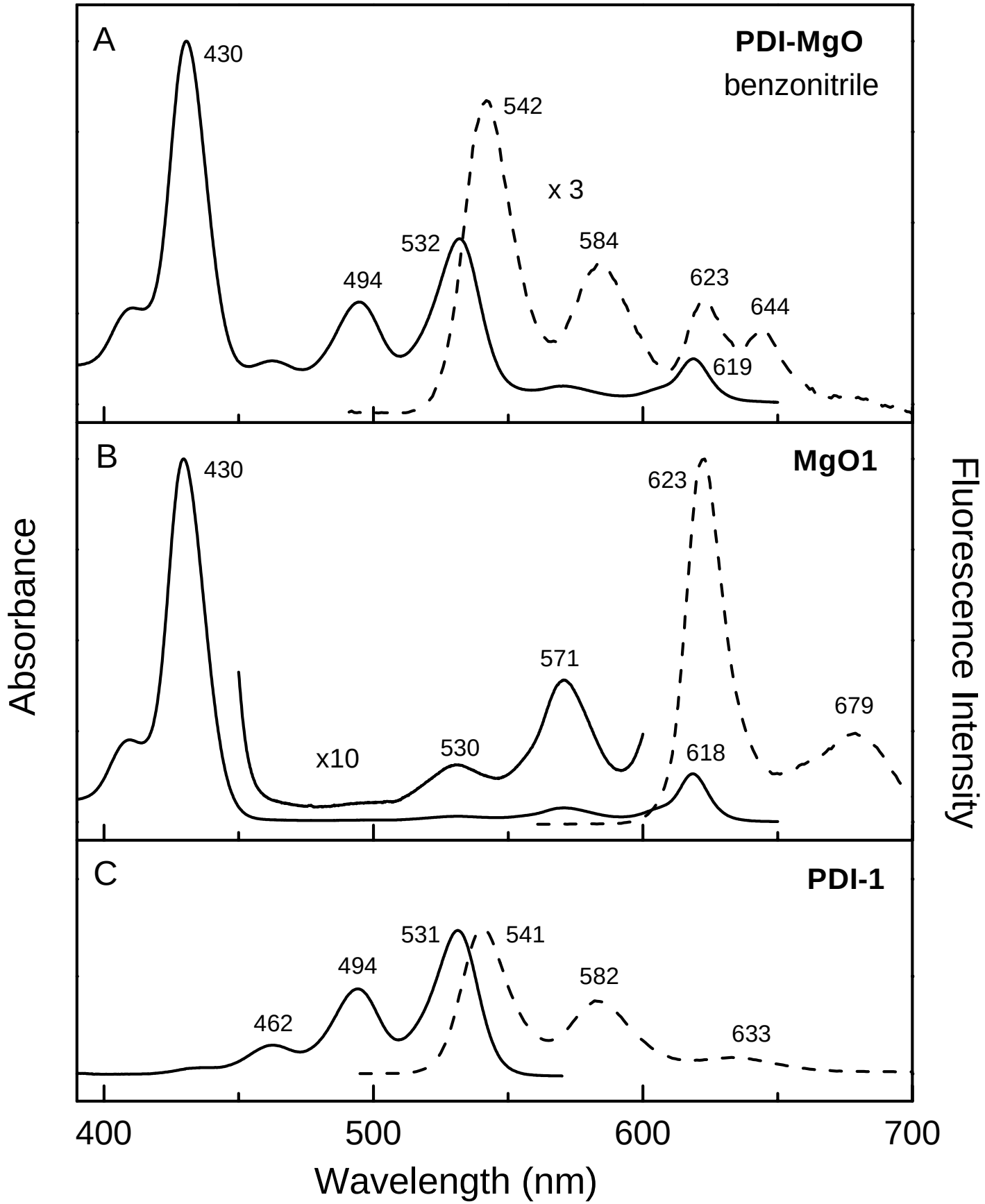
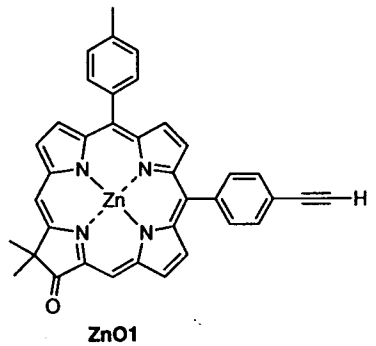
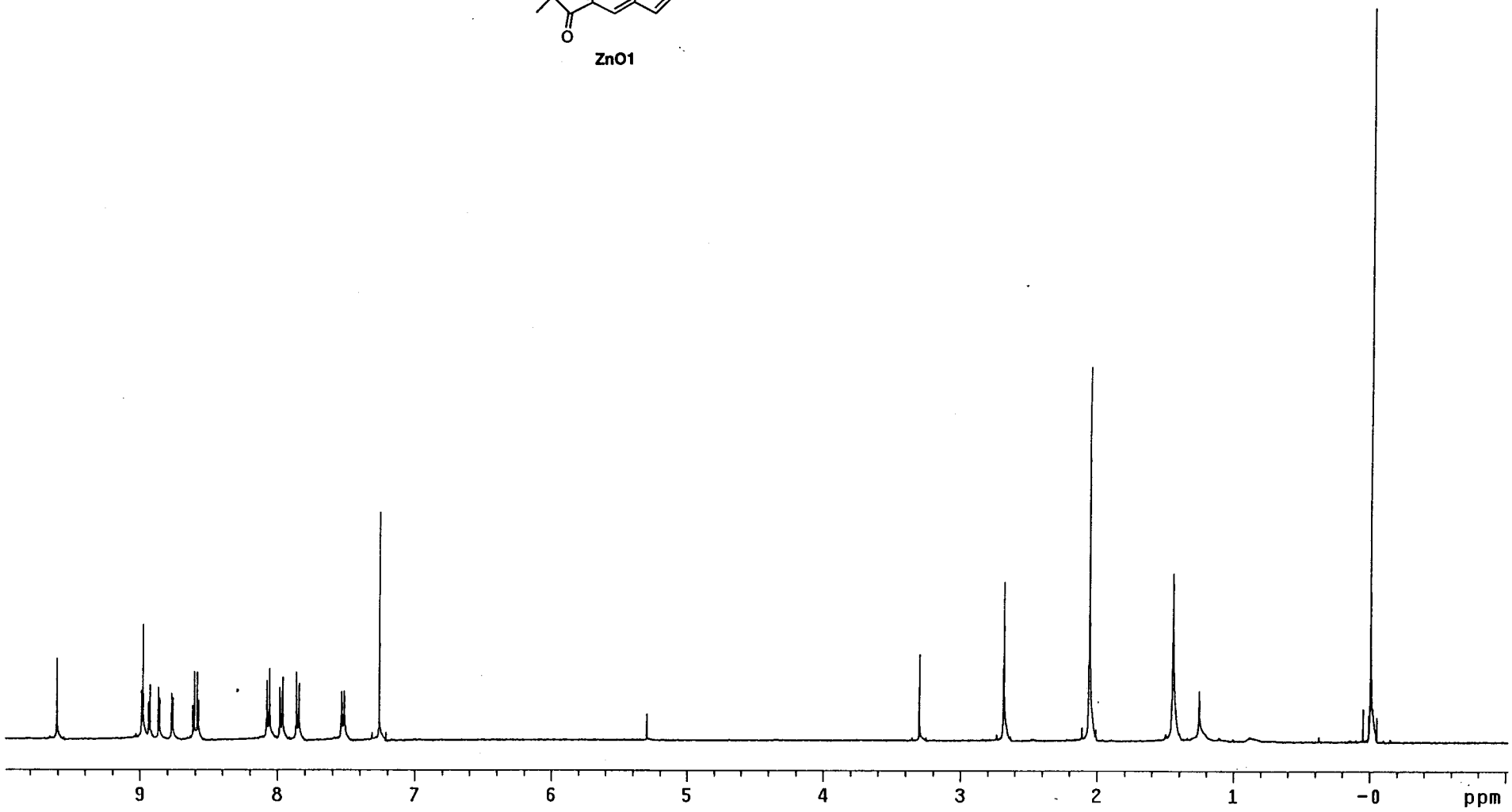

A
PDI-MgO
benzonitrile
430
542
x 3
532
584
494
623
644
619
B
MgO1
430
623
571
679
x10
530
618
C
PDI-1
531
541
494
582
462
633
Absorbance
Fluorescence Intensity
400
500
600
700
Wavelength (nm)

Figure SI-6



ZnO1



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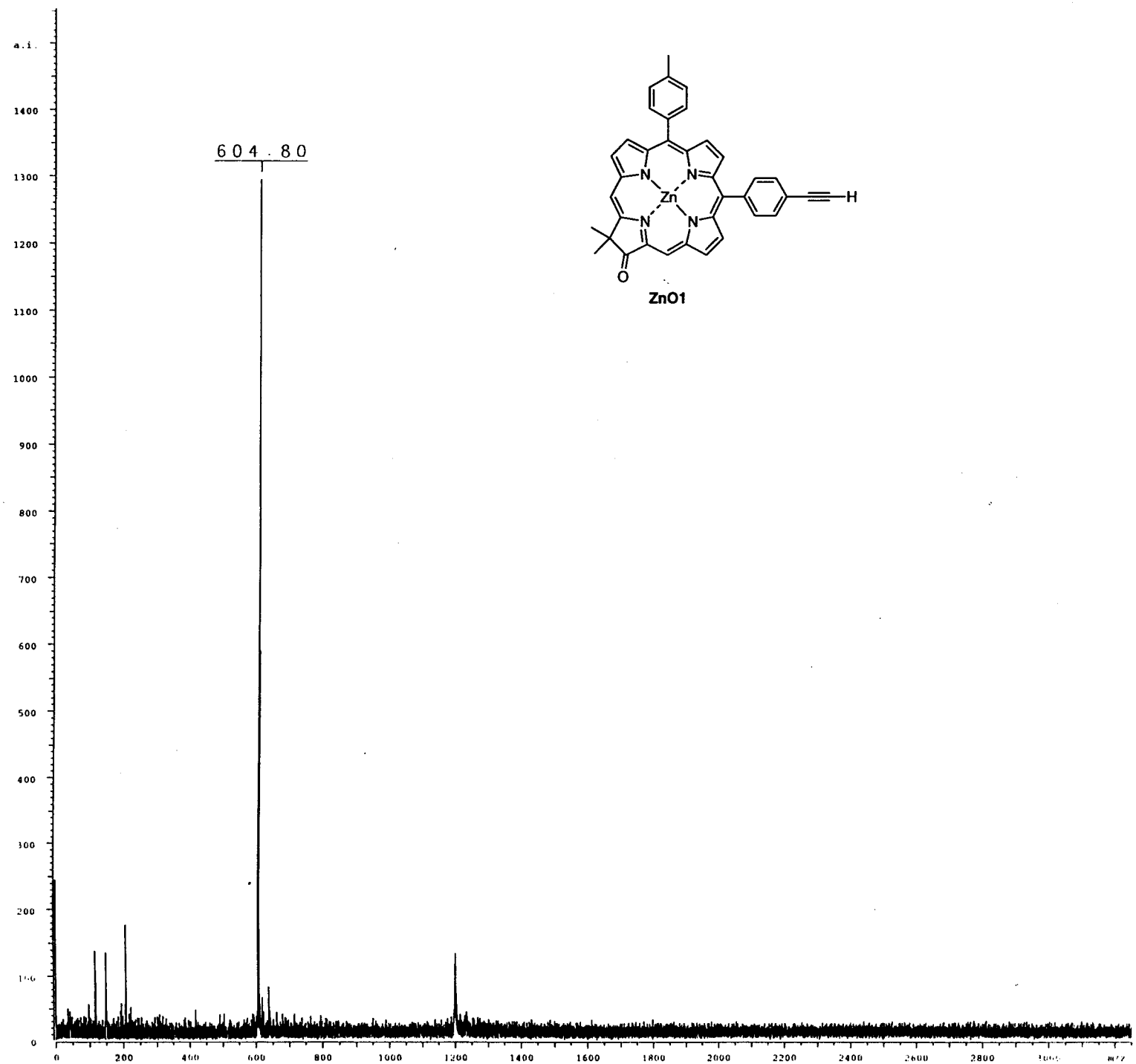

ZnO1

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Uis2               18.70  [kV]
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Ulens               7.50  [kV]
Uhimass            10.00  [kV]
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GDEDLY  short
DEFLON  no
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LLNSBND no
UIS2BND no
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DPMASS           700.00  [Da]
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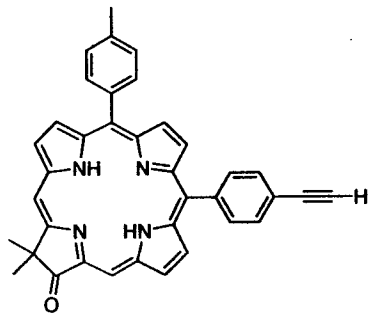
Figure SI-8



FbO1

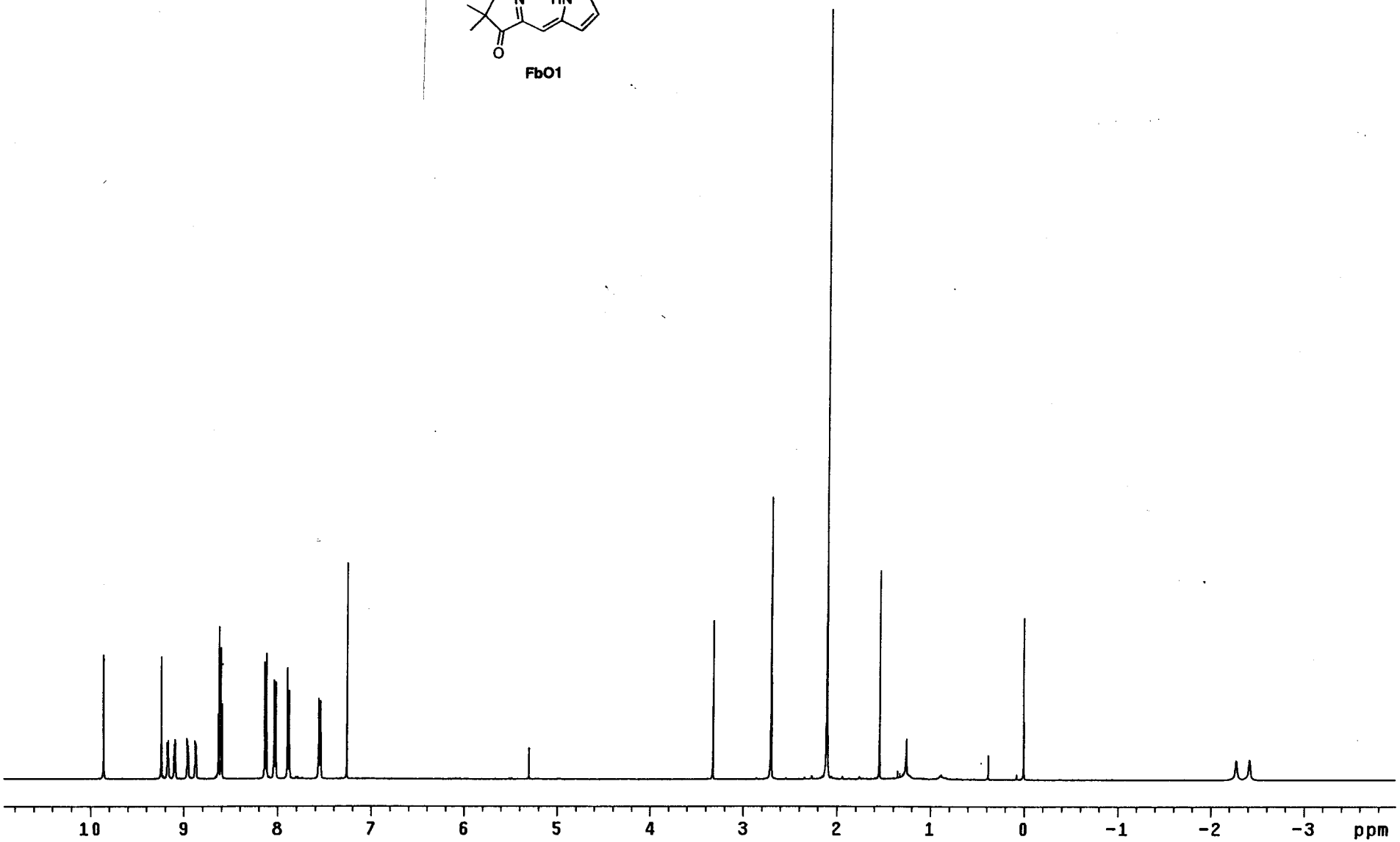
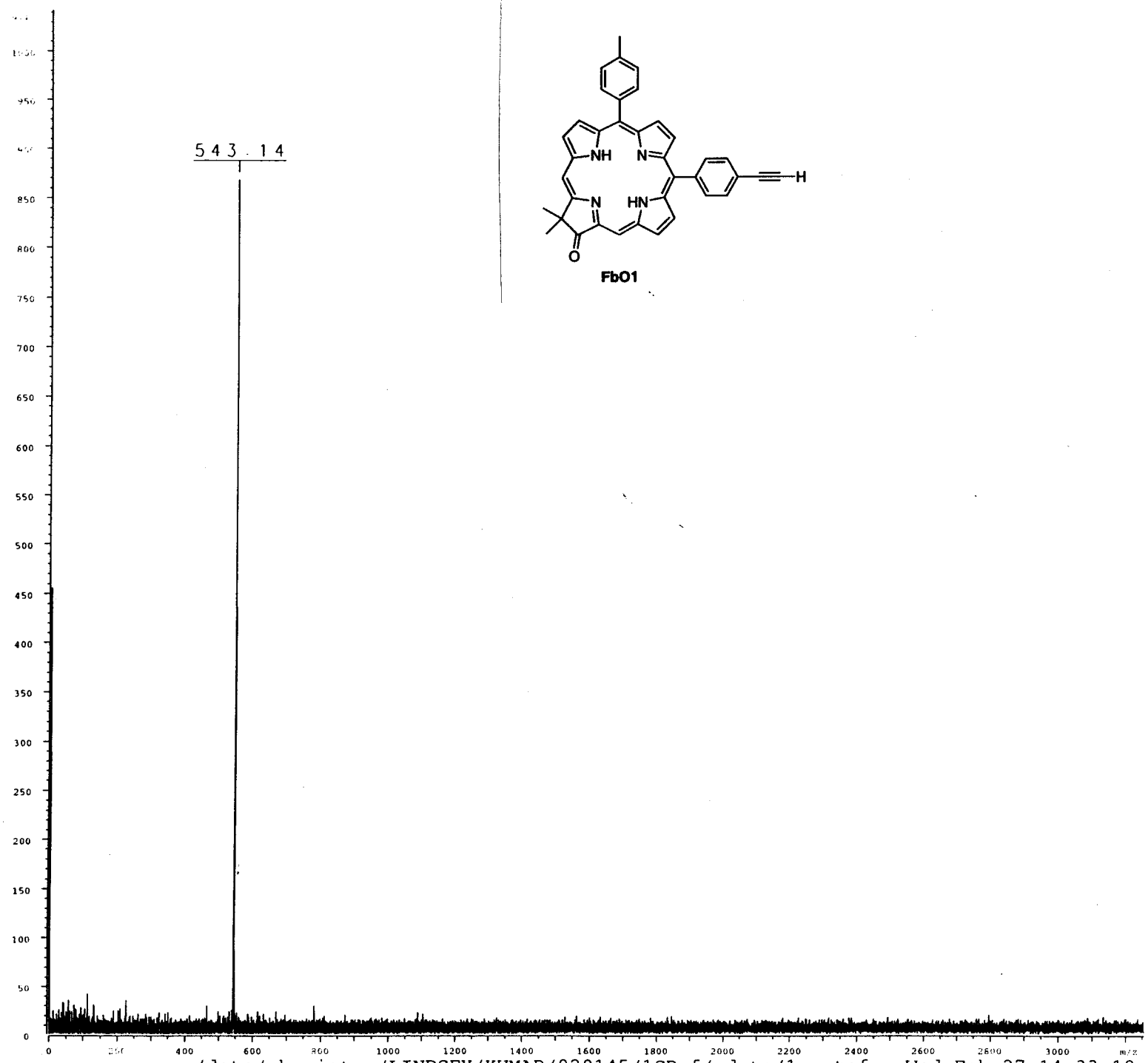


Figure SI-9



FbO1

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RefPul1             0.00   [kV]
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UdetR               0.00   [kV]
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REPHZ               1.00   [Hz]
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ML2              333.982
ML3                0.000
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GDEDLY  short
DEFLON  no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1           510.84
DPMASS           700.00   [Da]
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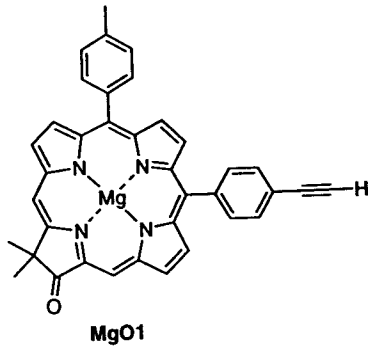
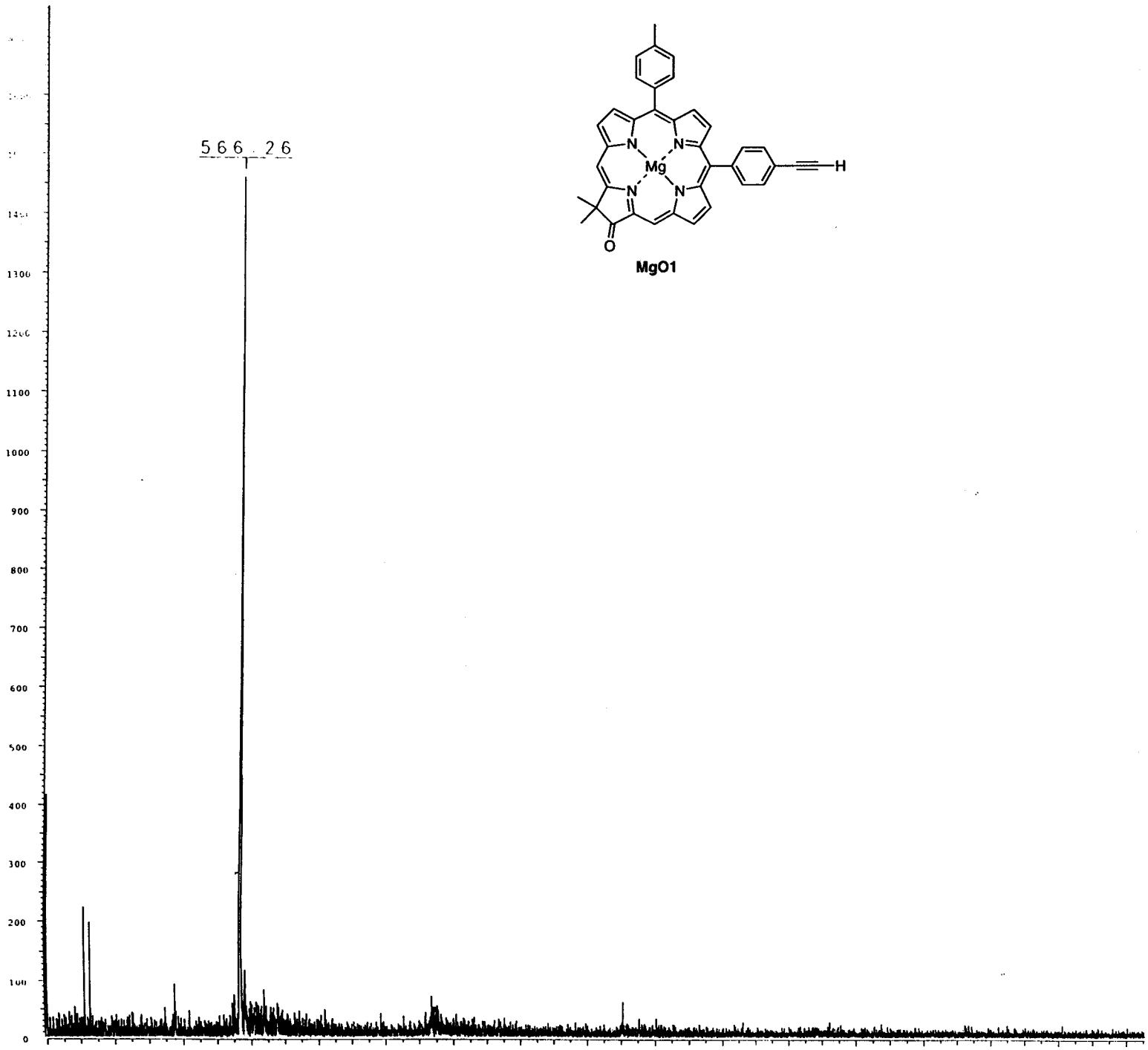


MgO1

Figure SI-11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Uis2 18.70 [kV]
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Ulens 7.50 [kV]
Uhimass 10.00 [kV]
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ML2 333.982
ML3 0.000
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GDEDLY short
DEFLON no
RLNSBND no
LLNSBND no
UIS2BND no
DPCAL1 510.84
DPMASS 700.00 [Da]
RBNDVAL 0.33
LBNDVAL 0.28
IS2BNDV 0.91
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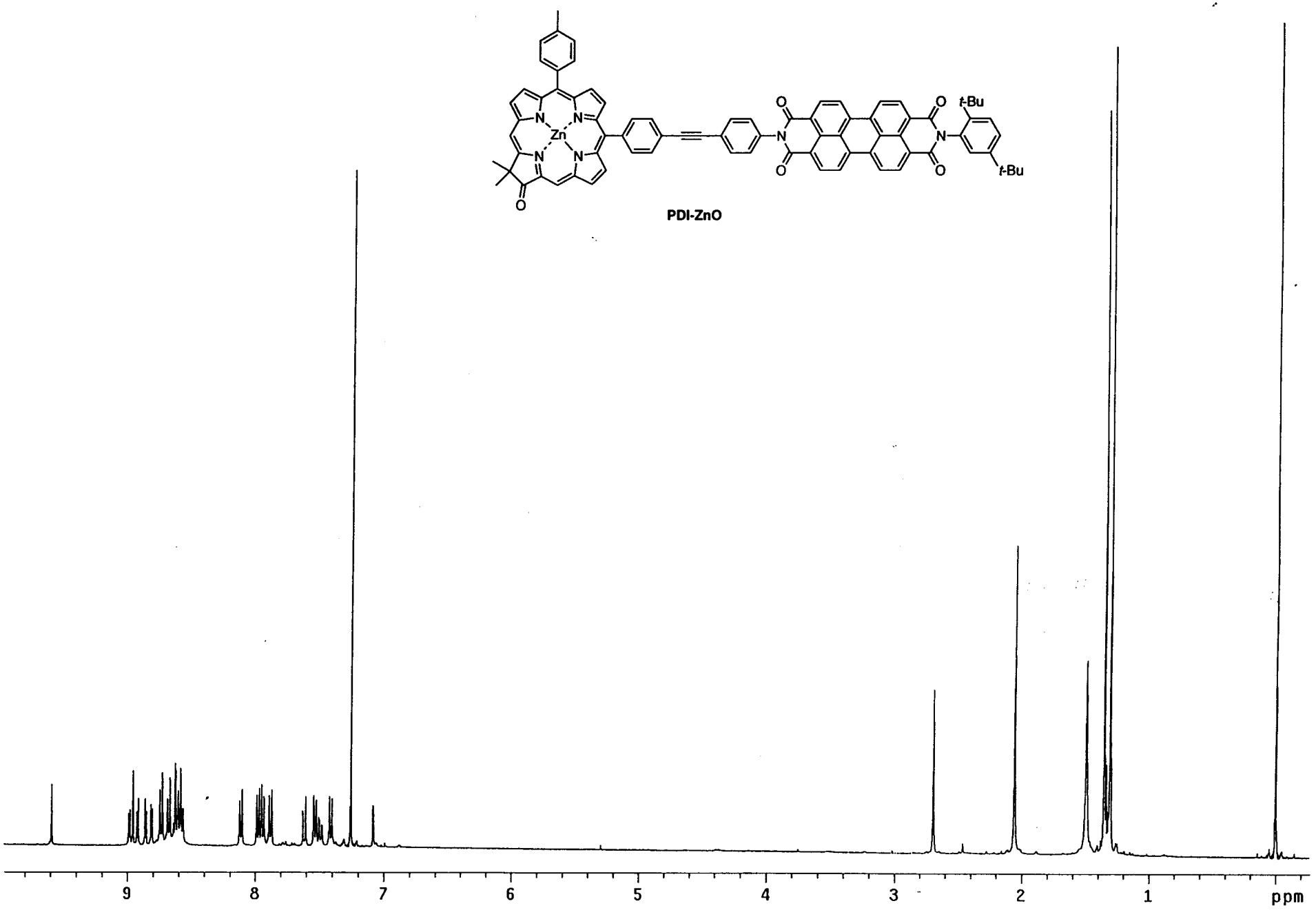
Figure SI-12



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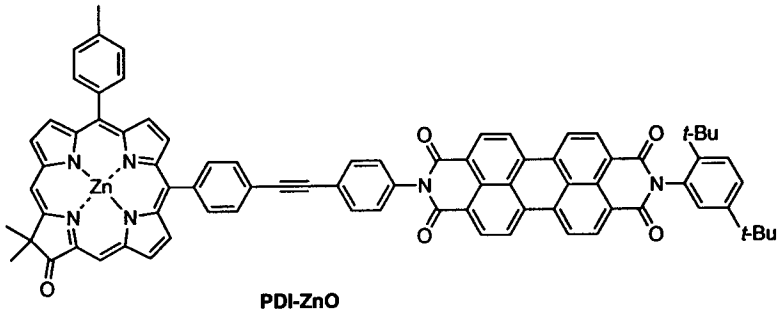

PDI-ZnO


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ML2              333.962
ML3                0.000
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DEFLON  no
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LLNSBND no
UIS2BND no
DPCAL1           510.84
DPMASS           700.00  [Da]
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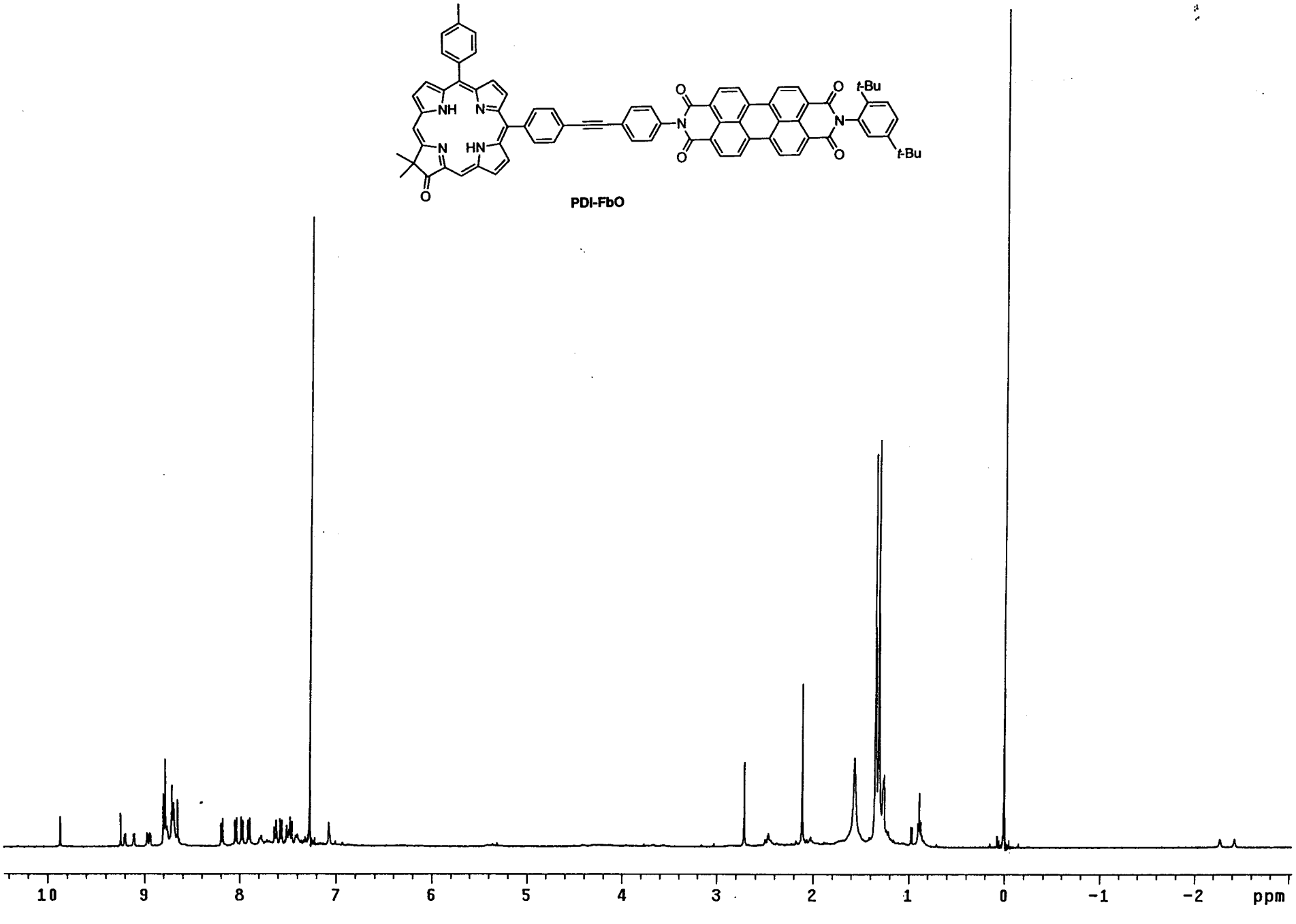
Figure SI-14



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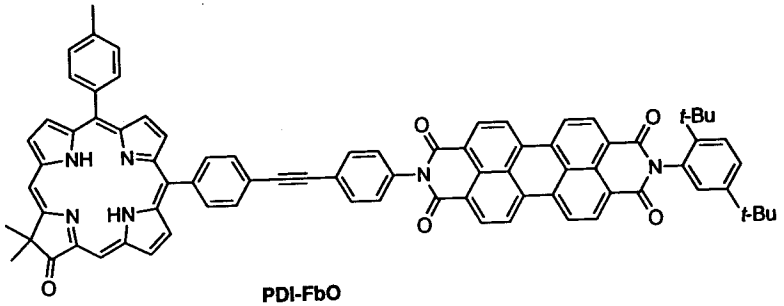

PDI-FbO


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LLNSBND no
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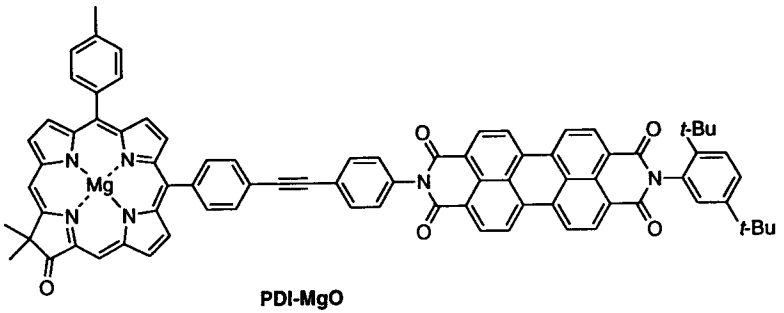
Figure SI-16



PDI-MgO

Figure SI-17

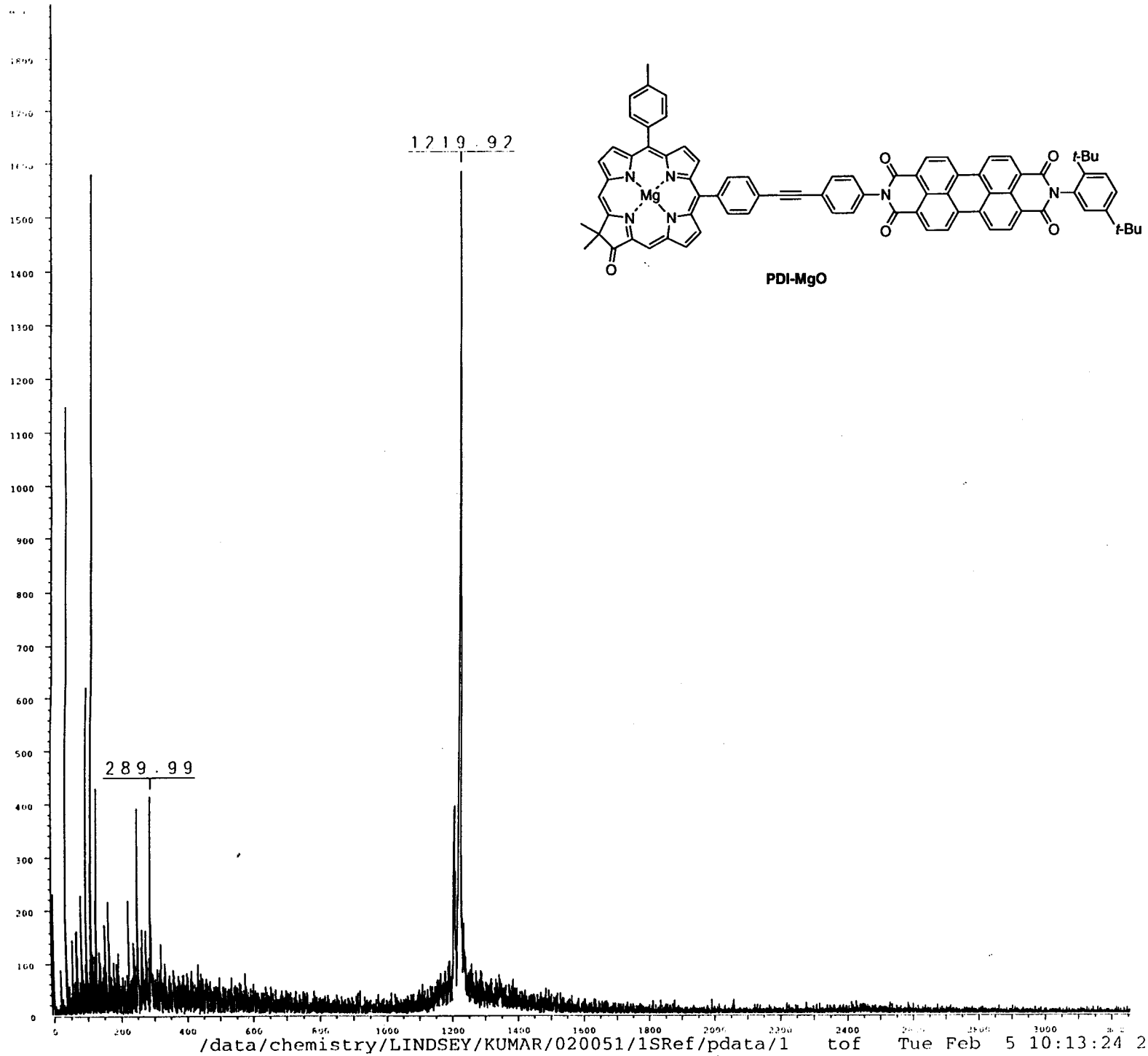

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Figure SI-18