Supporting Information

Preparation of Copper Ion Complex of Sterically Congested Diphenyldiazomethanes Having Pyridine Ligand and Characterization of Their Photoproducts

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General Methods.

$^1$H and $^{13}$C NMR spectra were recorded on JEOL JNM-AC300FT/NMR spectrometer in CDCl$_3$ with Me$_4$Si as an internal reference. IR spectra were measured on a JASCO-Herschel FT/IR-600H spectrometer, and UV-vis spectra were recorded on a JASCO CT-560 spectrophotometer. The mass spectra were recorded on a JEOL JMS-600H mass spectrometer. Gel permeation chromatography (GPC) was carried out on a JASCO, Model HLC-01 instrument using UV-1570 as a detector. The GPC column was a Shodex H-2001. Thin layer chromatography was carried out on a Merck Kieselgel 60 PF254. Column chromatography was performed on silica gel for column chromatography or ICN for dry column chromatography. Unless otherwise noted, all the reagents employed in this study are commercial products and used after standard purification. Tetrahydrofuran, ethyl ether, toluene, and dioxane were purified by distillation from sodium/benzophenone and dichloromethane, carbon tetrachloride, and triethylamine were from calcium hydride.

Preparation of diphentldiazomethanes.

Bis{2,6-dimethyl-4-(4-pyridyl)phenyl}diazomethane $(4,4'$-DPy-1-N$_2$).

Bis(2,6-dimethyl-4-bromophenyl)methanol$^1$ (2.00 g, 5.05 mmol) was mixed with SOCl$_2$
(10 ml) and mixture was stirred at room temperature for one day. The excess SOCl2 was evaporated to give bis(2,6-methyl-4-bromophenyl)chloromethane as a brown solid in 93% yield; 1H-NMR (300 MHz; CDCl3; Me4Si) δ 2.29 (s, 4H), 6.51 (s, 1H), 7.15 (s, 4H).

Since the chloromethane was found to be unstable, it was used without further purification.

A solution of the chloromethane (1.95 g, 4.70 mmol) in anhydrous 1,4-dioxane (30 ml) was added slowly to a mixture of ethyl carbamate (11.25 g, 126.3 mmol) and AgBF4 (1.48 g, 7.58 mmol) heated at 60 °C under vigorous stirring and the mixture was stirred at 100 °C for one day. The mixture was then filtered and the filtrate was extracted with CHCl3. The organic layer was washed with H2O to remove dioxane, dried (Na2SO4) and evaporated under reduced pressure. The resulting brown semisolid was chromatographed on silica gel column eluted with CH2Cl2-n-hexane (1:1). Ethyl N-bis(2,6-dimethyl-4-bromophenyl)methylcarbamate was obtained as a white solid in 80% yield; 1H-NMR (300 MHz; CDCl3; Me4Si) δ 1.25 (t, J = 7.1 Hz, 3H), 2.14 (s, 12H), 4.15 (q, J = 7.1 Hz, 2H), 4.89 (d, J = 7.9 Hz, 1H), 6.24 (d, J = 7.9 Hz, 1H), 7.11 (s, 4H); EIMS m/z (relative intensity) 471 (M+4, 33), 468 (M+2, 62), 466 (M+, 31), 389 (12), 387 (11), 211 (100); HRMS calcd for C20H23Br2NO2 467.0095, found m/z 467.0153.

To a mixture of the carbamate (500 mg, 1.06 mmol), 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane2 (880 mg, 4.30 mmol),
[1,1’-bis(diphenylphosphino)ferrocene]palladium dichloride dichloromethane complex: PdCl$_2$(dpff)$_2$·CH$_2$Cl$_2$ (100 mg, 0.11 mmol) and potassium phosphate (915 mg, 4.30 mmol) were added anhydrous 1,4-dioxane (25 ml) under Ar atmosphere and the mixture was stirred at 100 °C for two days. The mixture was then filtered and filtrate was extracted with Et$_2$O. The organic layer was washed with H$_2$O to remove dioxane, dried (Na$_2$SO$_4$) and evaporated under reduced pressure. The resulting brown semisolid was chromatographed on silica gel column eluted with ethyl ether. Ethyl N-bis{2,6-dimethyl-4-(4-pyridyl)phenyl}methylcarbamate was obtained as an yellow semisolid in 55% yield; $^1$H-NMR (300 MHz; CDCl$_3$; Me$_4$Si) δ 1.29 (t, $J$ = 7.2 Hz, 3H), 2.30 (s, 12H), 4.20 (q, $J$ = 7.0 Hz, 2H), 5.68 (d, $J$ = 8.1 Hz, 1H), 6.48 (d, $J$ = 8.1 Hz, 1H), 7.26 (s, 4H), 7.47 (d, $J$ = 4.6 Hz, 4H), 8.59 (brs, 4H); $^{13}$C-NMR (75.5 MHz; CDCl$_3$; Me$_4$Si) δ 14.7, 29.6, 54.8, 61.1, 121.3, 128.5, 136.5, 137.6, 138.7, 147.6, 150.0, 155.5; EIMS m/z (relative intensity) 465 (M$^+$, 79), 450 (100), 436 (40), 361 (70), 209 (89), 184 (76); HRMS calcd for C$_{30}$H$_{31}$N$_3$O$_2$ 465.2416, found m/z 465.2444.

A dinitrogen tetraoxide (2.76 g, 30.0 mmol) was bubbled into anhydrous carbon tetrachloride (15 ml) cooled to –20 °C. After sodium acetate (4.92 g, 60.0 mmol) was added to this mixture, a solution of the carbamate (530 mg, 1.34 mmol) in anhydrous carbon tetrachloride (30 ml) was added to the mixture at –20 °C and the mixture was
stirred for two hours at room temperature. The reaction mixture was poured into crush ice, and the mixture was added 5 % NaHCO₃ aqueous solution, extracted with carbon tetrachloride, and the organic layer was washed with H₂O, dried (Na₂SO₄) and evaporated.

**Ethyl N-nitroso-N-bis[2,6-dimethyl-4-(4-pyridyl)phenyl]methylcarbamate** was obtained as a khaki semisolid in 72% yield; ¹H-NMR (300 MHz; CDCl₃; Me₄Si) δ 1.29 (t, J = 7.2 Hz, 3H), 2.08 (s, 12H), 4.39 (q, J = 7.0 Hz, 2H), 6.95 (s, 1H) 7.27 (s, 4H), 7.49 (d, J = 5.9 Hz, 4H), 8.63 (d, J = 4.7, 4H).

All the following operations were carried out in dark room. To stirred and cooled solution of the nitroso-carbamate (480 mg, 0.97 mmol) in anhydrous THF (25 ml) was added t-BuOK (300 mg, 2.64 mmol) at –20 °C under Ar atmosphere and the mixture was stirred for one day at room temperature. The mixture was extracted with Et₂O, washed with water, dried (Na₂SO₄) and evaporated. The resulting orange solid was purified by repeated chromatography on a gel permeation column with CHCl₃.

**Bis[2,6-dimethyl-4-(4-pyridyl)phenyl]diazomethane (4,4’-DPy-1-N₂)** was obtained as orange solids in 17% yield; ¹H-NMR (300 MHz; CDCl₃; Me₄Si) δ 2.22 (s, 12H), 7.52 (brs, 4H), 8.66 (brs, 4H); ¹³C-NMR (75.5 MHz; CDCl₃; Me₄Si) δ 21.0, 58.8, 121.4, 127.5, 130.1, 136.9, 137.9, 147.5, 150.2; IR (NaCl, cm⁻¹) 2042(νC=N₂).
To a mixture of ethyl N-(2,6-dimethyl-4-tert-butylphenyl)(2,4,6-tribromophenyl)methylcarbamate³ (200 mg, 0.35 mmol), 2-(4-pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaborolane² (230 mg, 1.12 mmol), [1,1’-bis(diphenylphosphino)ferrocene]palladium dichloride dichloromethane complex: \( \text{PdCl}_2(\text{dpff})_2CH_2Cl_2 \) (32 mg, 0.039 mmol) and potassium phosphate (233 mg, 1.10 mmol) were added anhydrous 1,4-dioxane (5 ml) under Ar atmosphere and the mixture was stirred at 110 °C for two days. After work-up as described above, ethyl N-(2,6-dimethyl-4-tert-butylphenyl){2,4-di(4-pyridyl)-6-bromophenyl}methyl-carbamate was obtained as a yellow semisolid in 11% yield (20.8 mg); \(^1\text{H-NMR} \) (300 MHz; CDCl\(_3\); Me\(_4\)Si) \( \delta \) 1.26 (s, 3 H), 1.27 (s, 9 H), 2.04 (s, 6 H), 4.06-4.09 (m, 2 H), 5.03 (d, \( J=8.6 \) Hz, 1 H), 6.34 (d, \( J=8.6 \) Hz, 1H), 6.85 (brs, 4 H), 7.22 (d, \( J=2.0 \) Hz, 1 H), 7.46 (dd, \( J=4.4 \), 1.7 Hz, 2 H), 7.92 (d, \( J=1.8 \) Hz, 1 H), 8.39 (brs, 2 H), 8.64 (dd, \( J=4.4 \), 1.5 Hz, 2 H, H\(_a\)); \(^{13}\text{C-NMR} \) (75.5 MHz; CDCl\(_3\); Me\(_4\)Si) \( \delta \) 14.6, 21.1, 31.2, 34.1, 55.7, 61.2, 121.3, 123.2, 124.6, 128.3, 133.2, 133.9, 137.5, 138.7, 142.0, 145.4, 149.1, 150.4, 151.0, 155.0; EIMS \( m/z \) (relative intensity) 573 (M\(^+\)+2, 49);\(^{56}\)71 (M\(^+\), 49), 492 (56), 490 (63); HRMS calcd for C\(_{32}\)H\(_{34}\)BrN\(_3\)O\(_2\) 571.1834 , found \( m/z \) 571.1835.
(2,4-DPy-1-N$_2$) was obtained from carbamate (34.8 mg, 0.061 mmol) according to the procedure described above as an orange semisolid in 13% yield (30 mg); $^1$H-NMR (300 MHz; CDCl$_3$; Me$_4$Si) $\delta$ 1.25 (s, 9 H), 1.93 (s, 6 H), 6.78 (dd, $J=5.9$, 1.7 Hz, 2H), 6.82 (s, 2 H), 7.32 (d, $J=2.0$ Hz, 1 H), 7.49 (dd, $J=6.1$, 1.7 Hz, 2 H), 8.03 (d, $J=2.0$ Hz, 1 H), 8.26 (dd, $J=5.9$ Hz, 2 H), 8.67 (dd, $J=6.1$, 1.7 Hz, 2 H); $^{13}$C-NMR (75.5 MHz; CDCl$_3$; Me$_4$Si) $\delta$ 21.1, 31.2, 34.2, 65.8, 124.9, 125.2, 125.6, 127.8, 132.4, 136.1, 137.0, 137.5, 141.6, 145.4, 148.7, 150.5, 151.4; IR (NaCl, cm$^{-1}$) 2051($\nu$C=N$_2$).

REFERENCES


Analytical and spectroscopic data of photoproducts from diazo compounds

Photoproducts from 4,4’-DPy-1-N$_2$ and 2,4-DPy-1-N$_2$. 
The following compounds were isolated by photolysis of 4,4′-DPy-1-N₂ and 2,4-DPy-1-N₂.

**Bis{2,6-dimethyl-4-(4-pyridyl)phenyl} Ketone (4,4′-DPy-1-O).** mp 187.5-188.5 °C; 
^{1}H-NMR (300 MHz; CDCl₃; Me₄Si) δ 2.29 (s, 12H), 7.35 (s, 4H), 7.53 (brs. 4H), 8.71 (brs. 4H); ^{13}C-NMR (75.5 MHz; CDCl₃; Me₄Si) δ 21.0, 121.7, 127.8, 137.6, 139.7, 140.9, 147.3, 150.3, 201.6; EIMS m/z (relative intensity) 392 (M⁺, 17), 377 (100), 210 (8); HRMS calcd for C_{27}H_{24}N_{2}O 392.1889; found m/z 392.1925; IR (KBr, cm⁻¹) 3034w, 1657vs (νC=O), 1595, 1595vs, 1421w, 1289w, 930w, 849w, 822m.

**Tetrakis{2,6-dimethyl-4-(4-pyridyl)phenyl}ethene (2).** ^{1}H-NMR (300 MHz; CDCl₃; Me₄Si) δ 1.90 (s, 12H), 2.10 (s, 12H), 7.12 (d, J = 1.5 Hz, 4H), 7.21 (d, J = 1.5 Hz, 4H), 7.49 (brs, 8H), 8.61 (brs, 8H); ^{13}C-NMR (75.5 MHz; CDCl₃; Me₄Si) δ 22.6, 22.7, 121.2, 126.6, 127.8, 135.9, 139.2, 139.8, 141.9, 142.5, 147.3, 150.1; MALDI-TOF-MS calcd for C_{54}H_{49}N_{4} (M+H) 753.40, found m/z 753.49.

**8-Bromo-9-(4-tert-butyl-2,6-dimethylphenyl)-6-(4-pyridyl)-9H-2-azafluorene (3).** ^{1}H-NMR (300 MHz; CDCl₃; Me₄Si) δ 1.30 (s, 3H), 1.41 (s, 9H), 2.79 (s, 3H), 5.70 (s, 1H), 6.80 (s, 1H), 7.22 (s, 2H), 7.60 (s, 1H), 7.87 (s, 1H), 8.14 (s, 1H), 8.50 (s, 1H), 8.70 - 8.80
(m, 4H); EIMS m/z (relative intensity) 484 (M+2, 48), 482 (M+, 50), 469 (100), 467 (96);

HRMS calcd for C_{29}H_{27}BrN_2  482.1356, found m/z 482.1326.
Figure S1. Absorption of transient products formed during irradiation of diazo compound 4,4'-DPy-1-N₂ in non-degassed benzene at room temperature recorded 10 µs after excitation. Inset shows the time course of the absorption at 430 nm (oscillogram trace).

Figure S2. Plot of the growth rate of the carbonyl oxide 4,4'-DPy-1-O₂ as a function of oxygen concentration.
Figure S3. (A) Transient absorption spectra obtained in LFP of azafluorene 3 in degassed benzene with a 308-nm excimer laser recorded 1, 5, 10, and 100 µs after the pulse. (B) Oscillogram traces monitored at 430 nm.