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# A Fluorescent Sensor for Rapid Detection of Nucleophile and Convenient Comparison of Nucleophilicity

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**ABSTRACT:** Although nucleophile (Nu) is associated with many important chemical reactions, there are no fluorescence sensors for Nu detection and even for calculation of its nucleophilicity up to present. In this study, we developed a fluorescent malononitrile-modified perylenediimide (MAPDI), which can selectively and rapidly react with nucleophiles, such as amines, amino acids and some inorganic anions, then to change its UV-vis absorption and fluorescence emission. Detection limits of MAPDI for different nucleophiles could be calculated to compare their strength of nucleophilicity. Furthermore, it was found that MAPDI could detect reductive inorganic anions. These results suggested that MAPDI might have a great potential in organocatalytic reactions, metal ion-catalyzed reactions, reactions of amines and other nucleophilic chemical reactions.

*KEYWORDS: Nucleophile, nucleophilicity, calculation, fluorescent, sensor*

## INTRODUCTION

Many chemical reactions of substrates in solution appear to involve both a nucleophilic reagent and an electrophilic reagent. With the pivotal position of nucleophilic chemical reactions in chemistry reactions, 'click' chemistry has become a valuable tool in many applications,[1] such as organocatalytic reactions[2-4] and metal ion-catalyzed reactions,[5, 6] which have been widely used to functionalize small molecules. Although many nucleophiles (Nus), such as hydrogen peroxide, hydrogen sulfide, glutathione, cysteine and homocysteine, have been well known to properly involve in many different and important biochemical processes.[6-8] Some Nus, such as Cyanide anion ($CN^-$), are extremely hazardous for physiological systems in human body. Therefore, many excellent fluorescence sensors have been developed to selectively detect different Nus from various reagents based on their nucleophilicity in nucleophilic reactions.[9-13]

Although many equations, such as Swain-Scott equation,[14] Ritchie equation,[15] Mayr-Patz equation[16] and unified equation[17], have been reported to measure nucleophilicity,[18] all of them are complicate. Therefore, fluorescence sensor with simplicity and sensitivity might be a more convenient and practical tool to measure nucleophilicity of Nu.

In this study, a fluorescent sensor-malononitrile-modified perylenediimide (MAPDI, Scheme 1) was successfully developed to selectively and rapidly detect Nus, such as amines, amino acids and some inorganic anions, based on their nucleophilic addition, in which the UV-vis absorption and fluorescence emission was changed. Additionally, MAPDI could also be used to compare nucleophilicity by naked eyes, which might be very potential in the development of new nucleophilic reactions.

## EXPERIMENTAL SECTION

**Chemicals.** 1, 6, 7, 12-Tetrachloroperylene-3, 4, 9, 10-tetracar-boxylic acid dianhydride was obtained from Beijing Wenhaiyang Perylene Chemistry (Beijing, China). 4-Hydroxybenzaldehyde (98%) and malononitrile (99%) were purchased from Alfa Aesar. All other solvents and reagents were purchased from commercial suppliers and used as received.

**Instruments.** Nuclear magnetic resonance (NMR) spectra were recorded on Bruker 400 (400 MHz 1H; 101 MHz $^{13}C$) spectrometer using $CDCl_3$ and DMSO-$d_6$ and MeOD as solvent at room temperature. Chemical shifts were reported downfield from 0.00 ppm using TMS as internal reference. Matrix-assisted laser-desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) were determined on AXIMA-CFR plus MALDI-TOF mass spectrometer. Mass spectra (MS) were measured with a XEVO-G2QTOF (ESI) (Waters, USA). The UV-Vis absorption spectra were recorded on a spectrophotometer (Cintra 20, GBC, and Australia). The corrected Fluorescence spectroscopic studies were performed on a fluorescence spectrophotometer (Horiba Jobin Yvon FluoroMax-4 NIR, NJ, USA) at room temperature (25 $^oC$). Fluorescence quantum yields (FQYs) were measured at room temperature by using an Edinburgh Instruments FLS 980 fluorospectrophotometer. Electronic paramagnetic resonance (EPR) measurements were performed on a JEOL JESFA200 apparatus.

**General synthesis and characterizations.** MAPDI was synthesized according to the synthetic routes

(Scheme 1). AL was obtained with the methods of previous literatures.[19] Corresponding characterizations were shown in the Supporting Information.

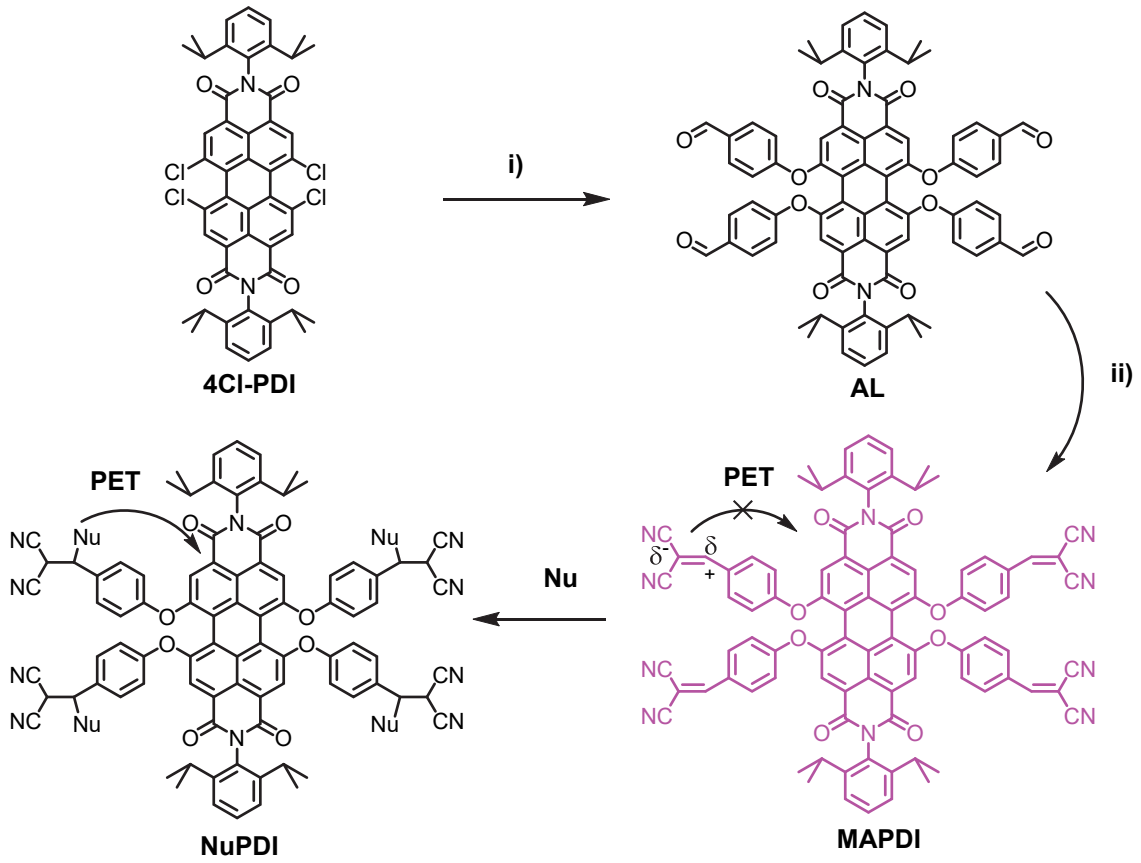
**Synthesis of MAPDI.** Solid $Al_2O_3$ (20 mg, 0.196 mmol) was added into a stirred solution of AL (12 mg, 0.01mmol) and malonitrile (10 mg, 0.12 mmol) in dry DMC (5 mL). The reaction mixture was stirred under nitrogen atmosphere at room temperature for 72 h. Chromatography on silica gel (ethyl acetate/ dichloromethane 1:20) yields a tawny solid. Yeild: 93%. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.35 (s, 4H), 7.88 (s, 8H), 7.74 (s, 4H), 7.50 (s, 2H), 7.34 (s, 4H), 7.08 (s, 8H), 2.68 (s, 4H), 1.15 (s, 24H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 162.46 (s), 160.09 (s), 157.88 (s), 154.08 (s), 145.45 (s), 133.03 (s), 129.83 (s), 127.22 (s), 124.05 (s), 121.64 (d, *J* = 42.5 Hz), 121.32 (s), 120.00 (s), 113.43 (s), 112.59 (s), 82.68 (s), 29.68 (s), 29.23 (s), 24.06 (s). MS (MALDI-TOF, m/z): Calcd for $C_{88}H_{58}N_{10}O_8$, 1383.46; Found, 1384.46 ($M+H^+$). Melting-point: 584.8 ºC.

**Synthesis of BMA.** Under an atmosphere of argon, benzaldehyde (1 g, 9.4 mmol), malononitrile (1.8 g, 28 mmol) and 5 mg alumina were dissolved in 15 mL THF.The reaction mixture was stirred, and the temperature was raised to 50 ºC. After stirred for 48 h at 50 ºC, the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography with dichloromethane as the eluting solvent to give a yellow solid BMA (1.37 g, 95%). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.7 Hz, 2H), 7.81 (s, 1H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 159.95 (s), 134.65 (s), 130.96 (s), 130.75 (s), 129.66 (s), 113.72 (s), 112.56 (s), 82.92 (s). HRMS (ESI-TOF, m/z): Calcd for $C_{10}H_6N_2$, 154.1550; Found, 155.0457 ($M+H^+$). Melting-point: 228.6 ºC.

**General Procedure for Nus Detection.** All UV-vis, fluorescence, and quantum yield measurements were carried out in DMSO or DMSO/water = 9/1. In a 2.5 mL tube, 1 mM MAPDI (4 μL) and 2 mL DMSO or DMSO/water = 9/1 were mixed, and then Nus was added to obtain a final concentration of 5 mM. Fluorescence spectra were recorded in the range from 40 to 760 nm with $\lambda_{ex}$ = 522 nm from a xenon lamp, and absolute emission quantum yields were determined accordingly.

## RESULTS AND DISCUSSION

**Design strategy of sensor.** The central perylenediimide (PDI) chromophore of MAPDI with high fluorescence quantum yield was used to improve the sensitivity of sensor. Double bonds could make MAPDI to specifically detect some Nus through addition reactions. When Nus attached MAPDI, its fluorescence would be quenched due to photoinduced electron transfer (PET) between the Nu and PDI. The synthesis of MAPDI was shown in Scheme 1. AL was synthesized from 4Cl-PDI according to literatures.[19] Then the obtained AL reacts with malonitrile to generate MAPDI, which is efficient under mild conditions. The detailed synthetic route and chemical structure of MAPDI were described in experimental section. The structures of MAPDI and intermediates were systematically characterized with $^1$H NMR, $^{13}$C NMR and TOF-MS (see TE Supporting Information).




**Scheme 1.** Synthesis approach and proposed sensing mechanism of probe MAPDI for nucleophilic reagents. i) hydroxybenzaldehyde, $K_2CO_3$, NMP, 80 °C, 50%; ii) malonitrile, $CH_2Cl_2$, r.t., 93%.

**Spectral properties.** As shown in Figure S1 (supporting information), MAPDI had main absorption peaks at 336 nm, 444 nm, 525 nm and 561 nm, respectively, and emission maximum at 600 nm with strong fluorescence (Φ = 0.48) in dimethyl sulfoxide, which was excellent for a sensitive fluorescence sensor. The absorption band (400-600 nm) is the characteristic absorption band of PDI moiety.[20,21] The extra absorption band peaking at 336 nm should belong to peripheral benzene-double bond-malonitrile moieties, which was confirmed through the synthesized benzene-double bond-malonitrile molecule (BMA, Figure 1A) to testify the speculation. 3D conformation of BMA shows that the benzene ring and dicyano-vinyl group are in a plane connected with double bond (Figure 1B). This planar construction BMA possesses UV-vis absorption from 300 nm to 400 nm peaking at 361 nm (Figure 1D). Additionally, the peripheral rigid structure makes double bond exposed (Figure 1C) and Nu can easily attach to double bond. When AL was modified with malonitrile to obtain MAPDI, a 25 nm blue-shifted was found in the absorption of BMA moieties with a slight red-shift in absorption of PDI moiety (Figure 1D). These results suggested that the PDI derivative MAPDI with high fluorescence intensity was successfully synthesized.

**Detection of amines and amino acids.** Because organic molecules with amino groups were used as Nus in many reactions,[22,23] reactivities of MAPDI with diverse amines were investigated according to their UV-vis and fluorescence spectra. It was found that MAPDI responded to various amines and amino acids (Figure 2) within a few minutes in DMSO at room temperature, in which the fluorescence intensity of MAPDI was decreased rapidly when amines and amino acids were added. Within only 10 seconds, the fluorescence intensity of MAPDI reached a plateau after the addition of *N*, *N*-diethylethylenediamine (Figure 3A). The detection time was much less than many fluorescence sensors.[10,24] When MAPDI was treated with various amines or amino acids in DMSO or in DMSO/$H_2O$=9:1 mixture solution, the absorption intensity of MAPDI at 336 nm was decreased and even disappeared (Figure S2 and S3) with a red-shifted, while no shape change of the characteristic absorption of PDI was observed. The decrease of MAPDI absorption intensity at 336 nm indicated that the peripheral small planar, conjugated and rigid structure was broken into flexible structure. When amine or

amino acid was added, MAPDI solution color was changed from pink to purple (Figure 3B). Because MAPDI displayed different decreases in fluorescence intensity upon reaction with amines and amino acids, degrees of quenching could be distinguished by naked eyes (Figure 3C). And the high fluorescence quantum yield or the fluorescence intensity of MAPDI could be decreased to as low as 0.0021-fold with added these Nus (Figure 3D), which indicated that MAPDI could sensitively detect Nus with amino groups.

**Detection of inorganic anions.** Inorganic anions also could take part in many chemistry reactions serving as Nus with or without catalyst.[9,25] the Among the tested inorganic anions as Nus to MAPDI, no change of UV-vis absorption and fluorescence was found when inorganic anion, such as $Cl^-$, $SO_4^{2-}$, $SCN^-$, $NO_3^-$ or $H_2PO_4^-$, was added, probably because these inorganic anions could not react or react very slowly with MAPDI at 5 mM. However, some inorganic anions, such as $SO_3^{2-}$, $HSO_3^-$, $S_2O_3^{2-}$, $HCO_3^-$, $HPO_4^{2-}$, $S^{2-}$, $ClO^-$ and $OH^-$, all made the UV-vis absorption on 336 nm and fluorescence intensity of MAPDI to decrease, as shown in Figure S3 and S4, which was similar to the results with added amines and amino acids. Additionally, when $NO_2^-$ was added into MAPDI solution, absorbance of MAPDI had a 24 nm red-shift from 336 nm to 360 nm without decrease on its fluorescence intensity. Therefore, MAPDI had excellent selectivity for Nu detection and could be used as a fluorescence Nu sensor.

**Studies on the detection mechanism.** As shown in Figure 4A, active amino group, thiol group and some inorganic anions could serve as nucleophile groups to attack the α-position of MAPDI to generate stabilized NuPDI. For example, $OH^-$ could attach the α-position of MAPDI to generate stabilized OH-PDI. The partial $^1H$ NMR spectra of the produced complex of MAPDI and excess $OH^-$ are shown in Figure 4B. The resonance signal at 7.74 ppm, corresponding to the vinylic proton (Ha), disappeared with a new signal at 5.33 ppm of the α-proton (Hb). Multiple peaks of benzene ring also shifted to around 7.0-7.5 ppm, which indicated that $OH^-$ was added to the vinyl group.[10] When $NO_2^-$ was added into MAPDI solution, they reacted due to their opposite changes, which could be confirmed by their UV-vis absorption and $^1H$ NMR spectra as shown in Figure S4C and S4D, the changes on $^1H$ NMR spectra of MAPDI-$OH^-$ and MAPDI-$NO_2^-$ were similar. Therefore, $NO_2^-$ should attach the double bond of MAPDI and replace dicyanomethane group to form a new structure with a new absorption at 360 nm.

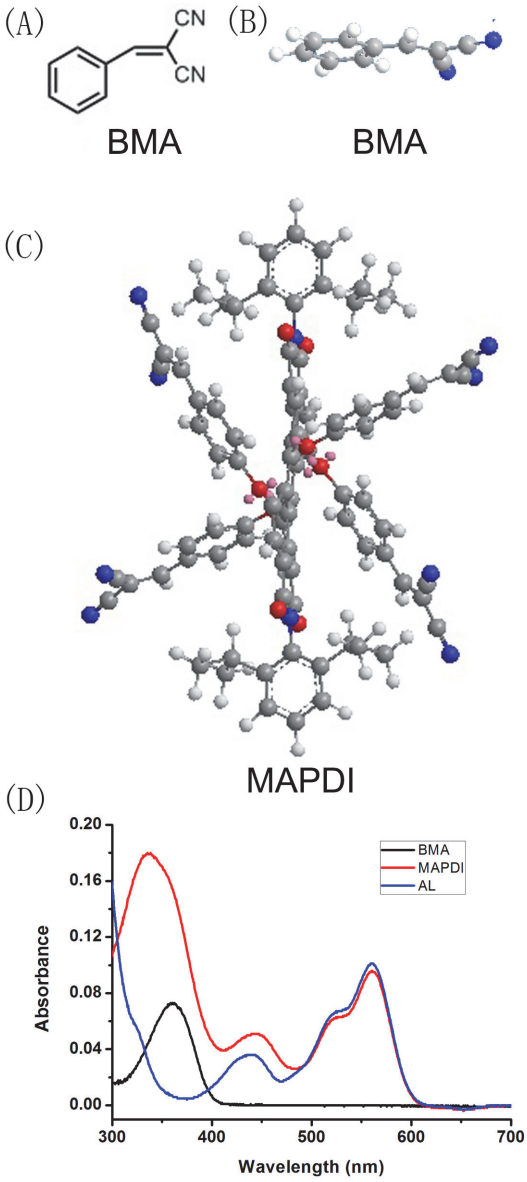



**Figure 1.** (A) Structure of BMA, (B) 3D conformation of BMA, (C) 3D conformation of MAPDI, (D) UV-vis absorption of BMA (5 μM), AL (2 μM) and MAPDI (2 μM) in DMSO at 25 °C.

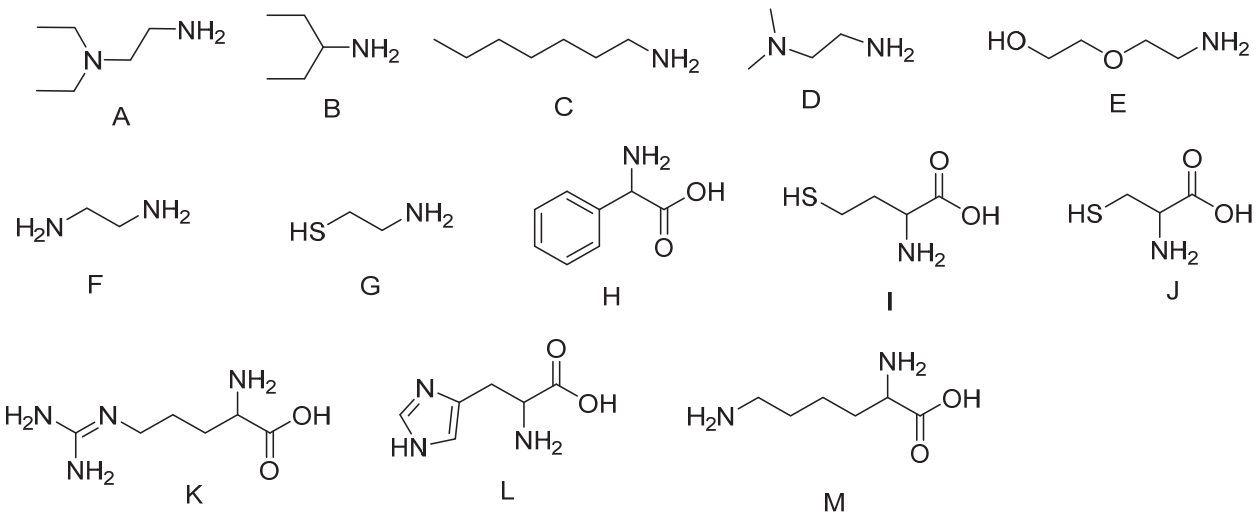



**Figure 2.** Structure of different amines (A: *N*, *N*-diethylethylenediamine, B: 3-aminopentane, C: 1-heptanamine, D: 2-dimethylaminoethylamine, E: 2-(2-aminoethoxy)ethanol, F: ethylenediamine, G: 2-amino-ethanethio, H: phenylalanine, I: homocysteine, J: cysteine, K: arginine, L: histidine, M: lysine).

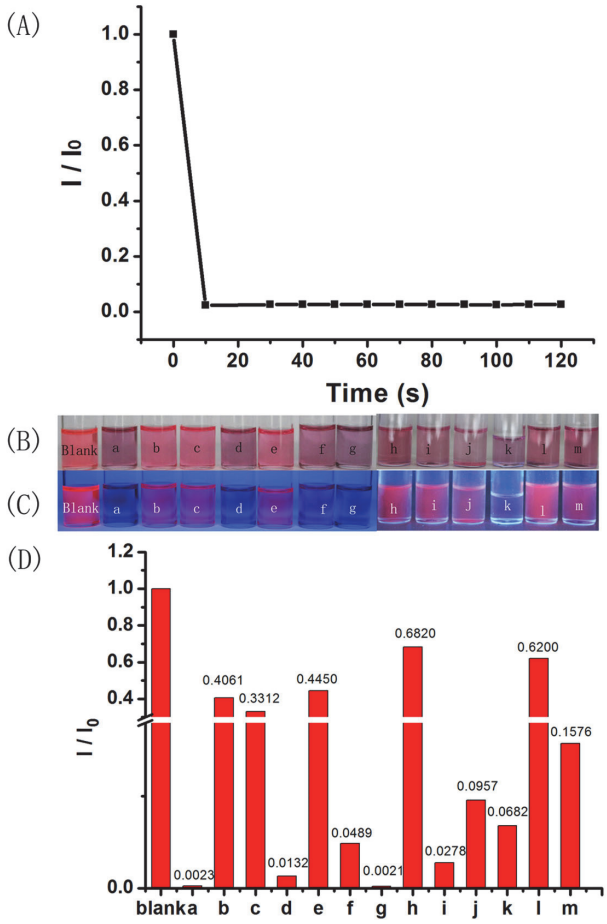



**Figure 3.** (A) The intensity maximum of MAPDI versus N, N-diethylethylenediamine (5 mM) at different time, (B) photographs, (C) fluorescence photographs (under UV light, $\lambda_{ex}$ = 365 nm) and (D) fluorescence intensity ratio ($I/I_0$, $\lambda_{max}$=600 nm, $\lambda_{ex}$ = 522 nm) of MAPDI (2 μM) in DMSO at 25 °C upon the addition of different amines (5 mM), measured after 1 min: a: *N*, *N*-Diethylethylenediamine, b: 3-aminopentane, c: 1-heptanamine, d: 2-dimethylaminoethylamine, e: 2-(2-aminoethoxy)ethanol, f: ethylenediamine, g: 2-aminoethanethio, h: phenylalanine, i: homocysteine, j: cysteine, k: arginine, l: histidine, m: lysine.

To confirm the mechanism of fluorescence intensity quenching, HOMO energy values of PDI, BMA and resulted structure of BMA with 1-heptanamine (BMA-H, Figure S5) were estimated and compared (Table S1). Because of the high HOMO energy of BMA-H, BMA-H could serve as an acceptor-excited photoinduced electron transfer (a-PeT) donor, resulting in a low fluorescence.[26,27] Because the HOMO energy values of BMA-$NO_2$ is lower than that of BMA, which can't serve as a-PeT donor to decrease the fluorescence intensity of MAPDI (Table S1). However, because $NO_2^-$ could serve as a Nu to react with MAPDI, there was a special change on UV absorbance of MAPDI when $NO_2^-$ was added into MAPDI solution, and the UV absorbance change on 336 nm was also very sensitive in the detection of different Nus.

**Nucleophilicity calculation.** The nucleophilicity can be compared through comparing the reaction time, in which a higher reaction rate corresponds to a higher nucleophilicity because the nucleophilicity of an electron donor is its relative reaction rate with a given electrophile.[18] The solution, temperature and other conditions are important for nucleophilic reactions, therefore, the comparison should be done under the same conditions. Typically, when the concentration of a Nu was below its detection limit (DL), the reaction rate could be considered as zero. The lower DL meant a higher nucleophilicity. Therefore, nucleophilicity could be compared through comparing DLs when the reactions rates were both very high. DL of MAPDI to each Nu was measured to distinguish their nucleophilicity as shown in Figure S9. The absorbance intensity change of MAPDI was linearly proportional ($R^2 > 0.95$) to the concentration of either amine or amino acid. As listed in Table 1, ethylenediamine had a higher nucleophilicity than 1-heptanamine because nucleophilicity of Nu with two amino groups was higher than that with one amino group. Since thiol was more active than amino in

nucleophilic addition,[28] nucleophilicity of 2-amino-ethanethio was higher than that of ethylenediamine. However, *N*, *N*-diethylethylenediamine and 2-dimethylaminoethylamine had higher nucleophilicity than other Nus, in which tertiary amine in *N*, *N*-diethylethylenediamine and 2-dimethylaminoethylamine might contribute to the higher nucleophilicity. As shown in Figure 3D, Figure S4 and Table 1, the changes of fluorescence intensity and DL results are in consistent with each other. Therefore, nucleophilicity of Nus could be roughly compared according to their fluorescence quenching abilities and accurately compared according to their DLs.

**Table 1.** DLs of MAPDI to amines and amino acids.

| [a]Amine | $R^2$ | DL (mol/L) |
|---|---|---|
| A | 0.999 | 7.9E-6 |
| B | 0.998 | 2.00E-5 |
| C | 0.988 | 9.6E-6 |
| D | 0.956 | 5.6E-6 |
| E | 0.963 | 1.16E-5 |
| F | 0.999 | 8.5E-6 |
| G | 0.978 | 4.4E-6 |
| H | 0.999 | 1.9572E-3 |
| I | 0.993 | 4.05E-5 |
| J | 0.994 | 9.29E-5 |
| K | 0.991 | 3.69E-5 |
| L | 0.996 | 1.7054E-3 |
| M | 0.956 | 4.88E-5 |

[a] A: N,N-Diethylethylenediamine, B: 3-aminopentane, C: 1-heptanamine, D: 2-dimethylaminoethylamine, E: 2-(2-aminoethoxy)ethanol, F: ethylenediamine, G: 2-amino-ethanethio, H: phenylalanine, I: homocysteine, J: cysteine, K: arginine, L: histidine, M: lysine.

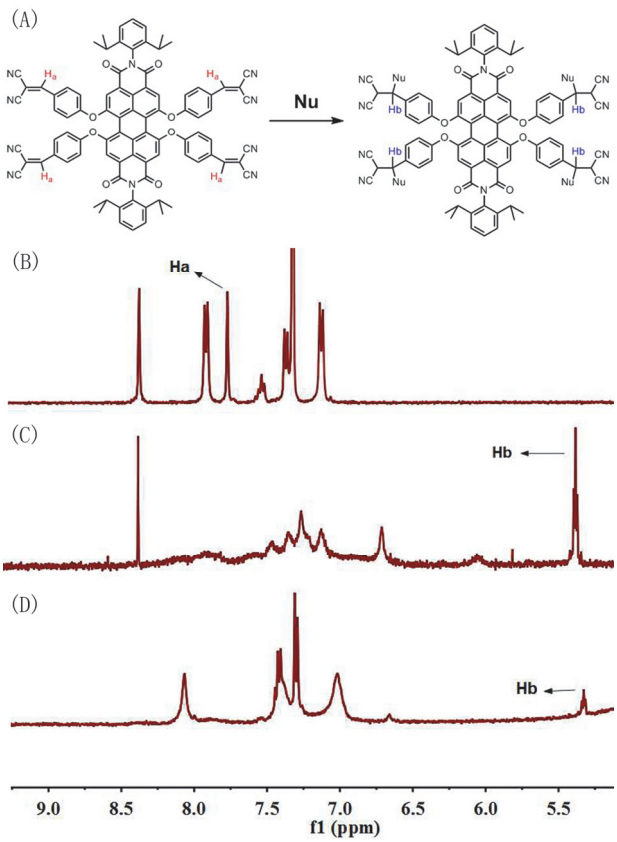



**Figure 4.** Proposed sensing mechanism of MAPDI to Nu (A), $^1$H NMR spectra of MAPDI (B) in $CDCl_3$, MAPDI-$OH^-$ (C) and MAPDI-$NO_2^-$ (D) in DMSO.

**Detection of reductive anions.** PDIs had been widely used in electron-transfer studies because they underwent reversible one-electron reduction at modest potentials to form stable radical anions.[29] $S^{2-}$ and $OH^-$ were common reductive inorganic anions in chemistry and electrochemistry, while $ClO^-$ could be ether reducing agent or oxidizing agent. As shown in Figure 5A-C, when the concentration of $S^{2-}$, $ClO^-$ or $OH^-$ was increased to 1.0 mM in MAPDI solution, the absorption band of PDI peaking at 445 nm, 525 nm or 562 nm was decreased, while the characteristic absorption bands of PDI radical anions[29-31] appeared at 700nm, 776-782 nm or 956 nm, respectively. And the formation of PDI radical anions was further confirmed with electron paramagnetic resonance (EPR) spectroscopy as shown in Figure 5D, in which $S^{2-}$, $ClO^-$ and $OH^-$ all displayed typical EPR signals, probably these three inorganic anions reacted with MAPDI through chemical reaction and give electron-deficient PDI electrons to generate delocalized radical anions through chemical or electrochemical reduction (Figure 5E). These results demonstrated that MAPDI could sensitively detect different inorganic anions and especially some reductive inorganic anions, such as $S^{2-}$, $ClO^-$ and $OH^-$.

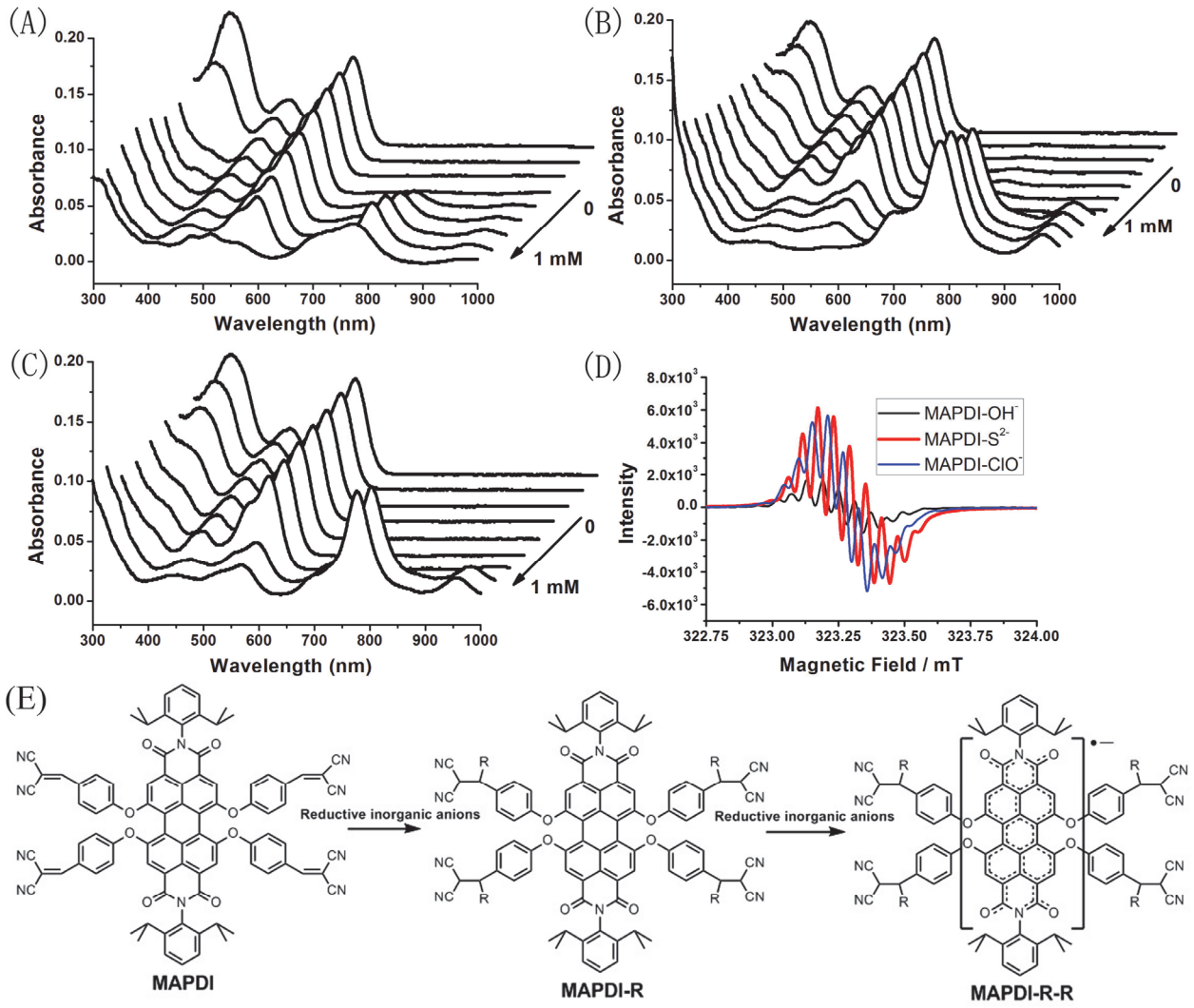



**Figure 5.** UV-vis absorption changes of MAPDI (2 μM) in 1 min after the addition of (A) $ClO^-$, (B) $S^{2-}$, (C) $OH^-$ (0-1 mM) in DMSO/water = 9/1; (D) EPR spectra of the radical anions generated from MAPDI (2 mM) within 2 min after the addition of $ClO^-$, $S^{2-}$, $OH^-$ in DMSO/water = 9/1; (E) proposed reaction mechanism of MAPDI with reductive inorganic anions.

## CONCLUSIONS

In summary, a rapid and sensitive nucleophilicity sensor MAPDI was successfully synthesized through the combination of small planar BMA and stable chromophore PDI. The proposed sensing and response mechanism have been confirmed by $^1$H NMR spectra and the comparison of HOMO energy values in which a nucleophilic addition of nucleophilic reagents on to the double bond of MAPDI. Furthermore, MAPDI could rapidly detect many Nus, including amines, amino acids and some inorganic anions within 1 min based on its fluorescence and UV-vis absorption changes. The nucleophilicity of Nus can be roughly compared according to the quenching degree of fluorescence intensity and accurately compared according to their DLs. To the best of our knowledge, this is the first time to detect Nus with a fluorescence sensor and conveniently compare nucleophilicity through the quenching degree of fluorescence intensity. Additionally, MAPDI could also be used as reducing inorganic anions sensor due to the PDI feature in high concentration of reductive inorganic anions. Therefore, MAPDI could open a new door to nucleophilic chemical reactions, including organocatalytic reactions, metal ion-catalyzed reactions, reactions of amines, etc.

## ASSOCIATED CONTENT

## AUTHOR INFORMATION

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**Supporting Information.** Details of synthesis, experimental methods and additional NMR, UV-Vis absorption and fluorescence emission properties, calculations and characterizations of MAPDI and BMA data.

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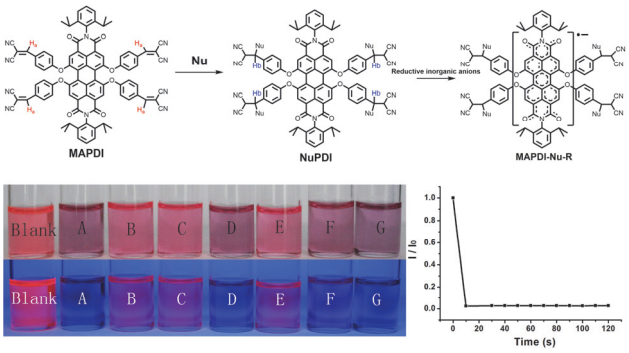
Nu
Reductive inorganic anions
MAPDI
NuPDI
MAPDI-Nu-R
Blank
A
B
C
D
E
F
G
Blank
A
B
C
D
E
F
G
I / I0
Time (s)