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Thiophene-fused-heteroaromatic diones as promising NIR reflectors for radiative cooling

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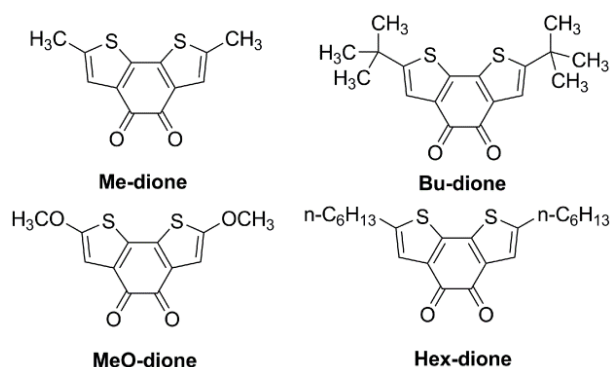
Abstract: Developing appropriate NIR reflective materials to combat near-infrared (NIR) heat radiation (700–2500 nm) from sun light for avoiding energy accumulation and reducing the energy consumption is urgent and highly desirable. In this research, four thiophene-fused-heteroaromatic diones have been used as basic reflectors to investigate the relationship between intrinsic molecular structures and Near Infrared (NIR) reflective properties. We found that the reflectance intensity can be readily tuned through adjusting the length of aliphatic side groups as well as the electron-donating groups. Since methoxyl (MeO-) substituted thiophene-fused-heteroaromatic dione shows the best performance in reflecting NIR, we employ it as a coating material to set up a glass model house for the comparison of the internal temperature difference with control, and a maximum of 12 °C lower is observed.

The construction of concrete buildings and roads to replace the originally-growing nature plants has a heavy contribution to the increasing temperature of densely-built urban environment, because the solar-energy-reflecting function of plants is substituted by the significant heat-accumulation effect on the surface of these man-made structures. Such a negative effect, arising from the indiscriminate destruction of natural vegetation and urban jungles, is known as 'urban heat island'.^[1–3] This phenomenon is mainly caused by near infrared (NIR) heat radiation (700–2500 nm) from sun light.^[4] Since 52% of solar energy (reaching the surface of the earth) is in the form of NIR radiation, which has no contribution to the colour of objects other than heat due to energy accumulation, it is highly desirable to develop appropriate NIR reflective materials to avoid energy accumulation and reduce the energy consumption from temperature regulatory system such as air conditioners.^[5] Evidence can be found in the report by Levinson et al, where the use of a NIR-reflecting roofing material could yield average annual cooling energy savings of 2.1 W/m² at peak power and the total cost saving up to \$5.87/m².^[6] Aside from their applications in heat management, NIR reflective materials have also been widely explored in military,^[7–10] plastic,^[11, 12] and ink industries,^[13, 14] which further confirms the significance in

conducting research in this field.

Generally, NIR reflecting materials can be categorized into two main groups: inorganic compounds and organic ones. Currently, the dominating reflectance pigments are inorganic materials such as titanium oxide,^[15] chromium oxide^[16] and rare earth oxide^[17]. Although the inorganic materials exhibit high reflectance due to their high refractive index,^[18, 19] these compounds face several unfavourable factors, such as unsatisfied aesthetic effects^[20] (e.g. TiO₂), toxicity issues^[21] (chromium oxide), and high cost due to the scarcity of rare earth elements. Such notorious disadvantages make organic materials more attractive because of their reduced toxicity or even nontoxic in some cases,^[22] low cost,^[23] and biocompatibility.^[24] More importantly, organic reflective materials normally have good processibility and miscibility with polymer matrixes, which make the dispersion much easier comparing to inorganic ones.^[25]

Although several organic pigment systems such as perylene bisimide (PBI) derivatives, Indigo dyes, copper phthalocyanine, and azo compounds have been explored,^[26] the relationship between molecular structures and NIR reflective properties has not been fully understood and the reported mechanism to explain the different behaviours of organic NIR reflecting materials is still unclear. Only in one theoretical study, Kaur et al suggested that pigments with sufficient symmetry (or less net dipole moment) and a small amount of functional groups (these groups should have high-frequency fundamental vibrations) may bring high reflectance in the NIR region.^[27] Unfortunately, the reported experimental results that can support this speculation are rare. This gap strongly encourages us to design a series of novel organic molecules and deeply understand the relationship between molecular structures and NIR-reflecting properties.



Scheme 1 Structures of the dione molecules studied in this work

In this work, a new conjugated system based on symmetrical thiophene-fused-heteroaromatic diones (**Scheme 1**) has been chosen as a model to investigate their NIR reflectance

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properties according to the following reasons: 1) comparing with widely-used organic pigments (e.g. PBI derivatives and copper phthalocyanine), the relatively smaller backbone might reduce the high-frequency vibrations and hence enhance the reflectance;^[27] 2) The attachment of different electron-rich/poor groups onto the molecular framework would result in different electronic environments and alter their UV-Vis absorption, which could bring different NIR reflectance;^[28] and 3) steric effect from different substituted groups (small, bulky, or long chain) might also cause different contributions to the NIR reflectance. Beside the above-mentioned criteria, these molecules also have some other charming factors such as high stability in air, good solubility in common solvents, and less cost due to their shorter synthetic routes and cheaper starting materials.

The thiophene-fused-heteroaromatic diones were prepared according to the reported procedure.^[29] Their UV-Vis absorption spectra were studied in DCM. As shown in **Fig. 1a**, Me-dione, Bu-dione and Hex-dione exhibited two main absorption regions (300 ~ 400 nm and 420 ~ 682 nm) with λ_{max} at 554 nm, which are in agreement with the reported UV-Vis absorptions of TMS-dione (**3a**).^[30] We also note that increasing the length of the substituted aliphatic group (e.g. Hex-dione, **Scheme 1**) does not bring significant change in the UV-Vis absorption spectrum comparing to Me-dione. Interestingly, when methyl group is replaced with methoxyl group, the λ_{onset} of MeO-dione red-shifts significantly from 680 nm to 852 nm and the λ_{max} moves from 554 nm to 627 nm, which might be due to the formation of a push-pull architecture.^[31, 32]

To investigate the possible intrinsic factors that affect the NIR reflectance of these molecules, we first conducted our research by following a reported method.^[33-35] As described in the experimental section, the dione molecules were mixed well with PMMA matrix to form uniform films for the comparison of their reflectance performance. Unfortunately, we noted that the reflectance of the controlled blank PMMA film varied from 8 to 40% (**Fig. S1**) depending on the evaporation rate, which implies that PMMA is not a good host for this reflectance study. Therefore, to avoid this issue, we decided to directly observe the reflectance nature of pure samples through drop-casting them onto glass slides.

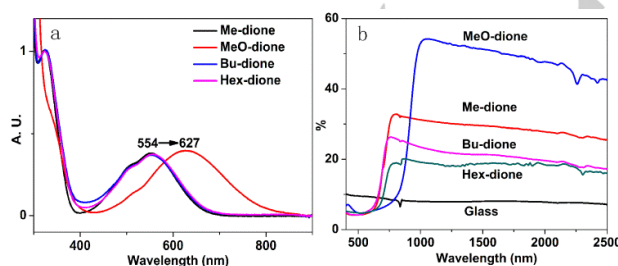


Figure 1 a) Normalized UV-Vis absorption and b) the reflectance spectra with same mol (1.2×10^{-2} mmol) of four molecules

Four films containing different dye molecules were fabricated by drop-casting 300 μL of each respective solution (the same concentration, 0.04 mol/L) on glass slides. Their reflectance spectra are measured and displayed in **Fig. 1b**. They are compared with the reference reflectance of 97% (**Fig. S2**). Me-dione, Bu-dione and Hex-dione exhibited the similar onset of enhanced reflectance (around 680 nm), which corresponded

well to the λ_{onset} of their UV-Vis absorption. Interestingly, when the length of the substituted chains increased from methyl to butyl to hexyl group, the reflectance gradually decreased, indicating that the reflectance ability can be tuned via changing the length of chains. More importantly, comparing with Me-dione, MeO-dione showed a drastically-increased reflectance from 830 nm due to its dramatic red-shifted UV-Vis absorption and an apparent higher reflectance up to 50% was observed. In addition, when the solution concentration increased to 0.08 mol/L, MeO-dione possessed an even higher reflectance (up to 60%) between 1000 nm and 1750 nm as shown in **Fig. S3**. To the best of our knowledge, this value is the highest reported reflectance for organic molecules till now.^[26, 33] Furthermore, the reflectance of the same film remained above 50% even at wavelength up to 2500 nm. These results suggest that the electron-donating MeO group might play a vital role in enhancing the reflectance, which could provide some useful clues for further designing new materials with strong reflectance. From the above discussion, it should be easily concluded that maintaining sufficient molecular symmetry, forming a push-pull architecture, and reducing the length of substituted aliphatic chains are helpful to enhance the reflectance of the as-resulted materials.

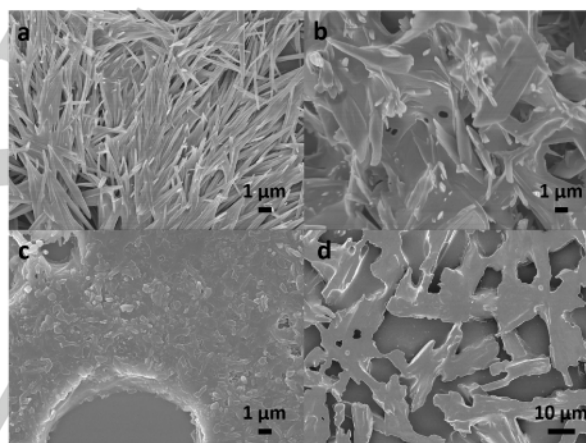


Figure 2 SEM taken on glass slide: a) Me-dione; b) MeO-dione; c) Bu-dione; d) Hex-dione

We also tried to understand how the morphology and crystallinity of organic dyes affect their reflectance behaviours. As shown in XRD spectra (**Fig. S4**), all four molecules exhibited the characteristics of high crystalline property except Hex-dione. The SEM images in **Fig. 2** revealed the distinct morphologies of Me-dione and MeO-dione, although they have similar molecular structures. Me-dione formed needle-like microcrystals with the size of 1 to 10 μm while MeO-dione was prone to form plate-like microcrystals. For Bu-dione, it formed crystalline particles with the size of ~ 1 μm while Hex-dione produced a completely different morphology with the aggregation size ranging from 10 to 50 μm . Although it has been discussed frequently that smaller crystal size responses to higher NIR reflectance value,^[13] our results didn't favour this conclusion because MeO-dione apparently has large crystal sizes than Me-dione and Bu-dione, but displayed higher reflectance. This result might hint that the morphologies may have less influence on the reflectance of these molecules. In fact, the intrinsically conjugated structure

and smaller functional groups should be key factors to obtain high reflectance intensity.

To quantitatively evaluate the performance of these diones as reflectance materials for cooling, we selected the best-performed MeO-dione as an example and built up a glass model house to test the internal temperature difference as illustrated in **Fig. 3a**. We constructed three closely-aligned empty chambers using glass slides. The middle chamber was insulated with Styrofoam to minimize heat diffusion and flanked by two empty chambers covered with glass and MeO-dione-coated glass as “roofs”, respectively. The entire set up was heat-insulated by Styrofoam to block heat exchange between the internal and the external of the houses. An artificial sunlight source was used to better mimic the real application. Thermocouples were placed inside the insulated empty chambers to measure the temperatures upon the irradiation of one simulated sun, and the temperature difference between two thermocouples was recorded.

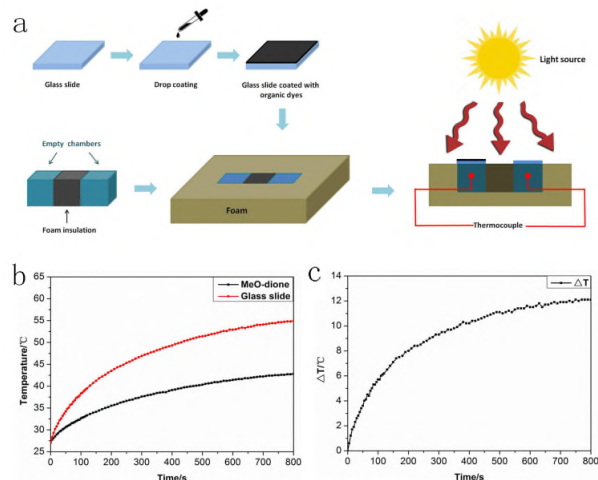


Figure 3 a) Schematic diagram for thermometer measurement; b) Internal temperatures of chamber coated with or without MeO-dione; c) Internal temperature difference between houses coated with or without MeO-dione.

Temperatures inside two chambers were $\sim 27^\circ\text{C}$ at the beginning of the measurement. When the artificial sun irradiated vertically on top of two houses, the internal temperature increased simultaneously due to the building up of the heat contributed from the NIR radiation. As shown in **Fig. 3b**, the pure glass-roofed and MeO-dione-coated glass-roofed chambers showed different temperature profiles under same irradiation. The temperature of the glass-roofed chamber increased more rapidly compared to the MeO-dione-coated glass roof during the initial irradiation period, indicating the strong NIR reflectance for MeO-dione compound. As the measurement continued, the increase for both curves slowed down gradually. **Fig. 3c** showed the temperature difference between the two chambers, which agreed with the temperature profiles, rapid ΔT at the beginning and reached a constant difference of 12°C as irradiation continued. It is apparent that MeO-dione can act as a potential cooling material.

To demonstrate the advantage of MeO-dione over the other inorganic pigments, the most-widely used NIR reflective material TiO_2 ^[36] and a commercially-available blue NIR reflective material

$\text{YIn}_{0.975}\text{Mn}_{0.025}\text{O}_3$ ^[37] were drop-casted on glass slides at the equivalent molar amount. Unfortunately, the films formed by TiO_2 (1.8 mg) and $\text{YIn}_{0.975}\text{Mn}_{0.025}\text{O}_3$ (6.0 mg) failed to cover the entire glass slides due to low loadings, as shown in **Fig. S5**. Thus, PDMS was used as a host. Because TiO_2 is white, which might have less applications in practical due to aesthetic reasons, it will be omitted for further measurement. The $\text{YIn}_{0.975}\text{Mn}_{0.025}\text{O}_3$ /PDMS film, fabricated with an equivalent molar amount of $\text{YIn}_{0.975}\text{Mn}_{0.025}\text{O}_3$ to MeO-dione, showed a 6°C temperature difference (**Fig. S6**), which indicated that MeO-dione showed a higher efficiency in cooling performance comparing to inorganic pigments at equivalent molar amount.

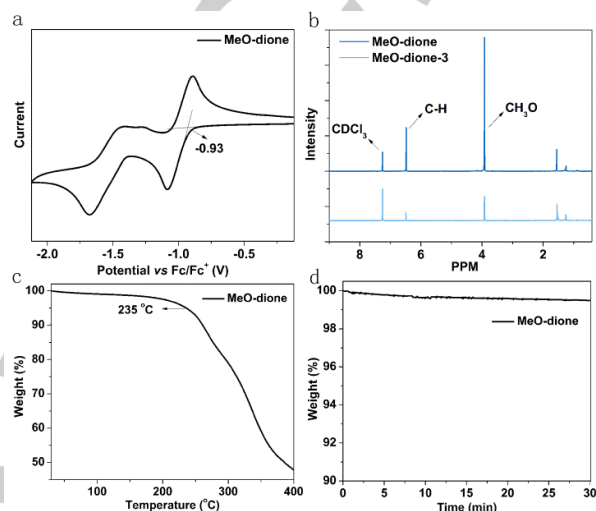


Fig. 4 a) CV of MeO-dione curve; b) NMR spectra of as-prepared MeO-dione and the sample (MeO-dione-3) subject to ambient environmental conditions for 3 months; c) heat ramp from room temperature to 400°C ; and d) isothermal heating of MeO-dione at 100°C in air for 30 mins.

Stability is a critical requirement for any NIR reflective materials. In order to evaluate the stability of MeO-dione, Cyclic Voltammetry (CV), Nuclear Magnetic Resonance (NMR), and Thermogravimetric Analysis (TGA) were conducted. The electrochemical properties of MeO-dione were investigated in a dry methylene chloride solution with $0.1\text{ M n-Bu}_4\text{NPF}_6$ as the electrolyte and ferrocene as the internal standard. The CV spectrum of MeO-dione was recorded in **Fig. S7**. As shown in **Fig. 4a**, MeO-dione exhibited an $E_{\text{red}}^{\text{onset}}$ of -0.93 V in comparison with Fc/Fc^+ , corresponding to a LUMO energy level of -3.87 eV according to the empirical formula $\text{LUMO} = -(E_{\text{red}}^{\text{onset}} + 4.80)\text{ eV}$. The as-obtained LUMO value is even lower than that of the air-stable product naphthalene diimide (-3.66 eV) measured by the same method,^[38] indicating the superior stability of MeO-dione in air. **Fig. 4b** shows the almost identical NMR spectra obtained for freshly-prepared MeO-dione and the one after exposure in air for 3 months. TGA was conducted in air with heat ramp from room temperature to 400°C and isothermal at 100°C (**Fig. 4c** and **Fig. 4d**). A 5% weight loss at 235°C and a 0.5% weight loss under isothermal at 100°C suggest its high environmental stability.

In conclusion, we have prepared four fused heteroaromatic dione compounds and investigated how the intrinsic factors of these four compounds to affect their NIR reflectance. We found that a highly-symmetric conjugation backbone with a push-pull architecture and smaller substituted groups can result in high reflectance value. Especially, MeO-dione exhibits an excellent

reflectance (up to 60%) as well as a significantly red-shifted reflectance comparing with other three molecules, indicating that the bathochromic shift of reflectance can be tuned through adjusting the electronic density on the conjugated framework. Moreover, when MeO-dione was demonstrated as a potential roof coating material in a glass model house, a maximum of 12 °C lower comparing with the control was observed. Clearly, our study should provide a guideline for the future design of efficient organic molecules with tunable NIR reflectance.

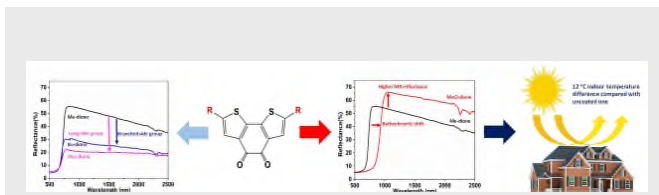
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Keywords: NIR reflectance • diones • radiative cooling • thermometer measurement • conjugated materials

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COMMUNICATION



Four thiophene-fused-heteroaromatic dione (benzo[1,2-b:6,5-b']dithiophene-4,5-dione) compounds were used to investigate the relationship between intrinsic molecular structures and Near Infrared (NIR) reflective properties. When MeO-dione was demonstrated as a potential roof coating material in a glass model house, a 12 °C lower was observed comparing with control.

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