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# One-Pot Synthesis and Structure-Property-Relationship of Aminomaleimides: Fluorescence Efficiencies in Monomers and Aggregates Easily Tuned by Switch of Aryl and Alkyl

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ABSTRACT: Organic fluorophores have attracted great interest owing to their wide applications. They usually contain an electron conjugated system with aromatic moiety and show high emission in dilute solutions but weaker or even no emission upon



aggregation. Here, a simple one-pot three-component reaction (3CR) (method I) for the synthesis of various di- and mono-substituted aminomaleimides (DAMIs and MAMIs) has been developed, and the reported 3CR (method II) has been found to be efficient only for the synthesis of MAMIs with R<sup>2</sup>=alkyl. 12 AMIs were designed and synthesized for investigation of the influence of structures on their optical properties in monomers and aggregates. It was found that alkyl MAMIs, alkyl DAMIs and aryl AMIs/DAMIs show very different fluorescence efficiencies in different solvents, and only MAMIs with butyl and oleyl show similar high emissions in powders to those in nonpolar solutions. Single-crystal structures indicate that their fluorescence efficiencies in aggregates mainly correlate with molecular packing modes. The efficient synthesis method, the sensitive fluorescence-on-off response to protic solvents or polar solvents, and the unusual high emissions of AMI without any aromatic moiety in both monomer and aggregates are expected to attract great interest in the fields of application and theory.

#### INTRODUCTION

Organic fluorophores have attracted great interest owing to their wide applications. They generally contain rigid

aromatic groups and are highly emissive in dilute solutions but less or even no emissive upon aggregation, which is frequently referred to as the aggregation-caused quenching (ACQ) effect. Since fluorophores are usually used in relative concentrated solutions or solid states, the ACQ effect becomes a thorny problem in many practical applications. Therefore, different methods have been developed to overcome the effect such as increasing distance by introduction of bulky substituents,<sup>2-4</sup> controlling J-aggregation<sup>5-7</sup> and cross-dipole molecular packing modes.<sup>8</sup> In 2001, a propeller-like fluorophore, 1-methyl-1,2,3,4,5-pentaphenylsilole, was found to be not emissive in solutions but strongly emissive upon aggregation, which was termed as aggregation-induced emission (AIE).<sup>9</sup> The AIE characteristics overcome the ACQ effect fundamentally. For the last decade, AIE compounds have showed to be of great advantages in many areas such as OLEDs<sup>10,11</sup> chemo/biosensors,<sup>12-16</sup> and bioimaging.<sup>17,18</sup> Experimental results prove that AIE fluorophores generally possess twist molecular structures with aromatic rotors that efficiently prevent  $\pi$ - $\pi$  stacking.<sup>19-22</sup> In spite of their comprehensive applications, the AIE compounds are limited to the application in solutions because they are not emissive in monomers. Therefore, the fluorophores with high fluorescence efficiency in both dilute solutions and aggregates are expected to have wider scope of applications and still remain an interesting topic. For example, professor Yuan et al have tried to obtain high fluorescence efficiencies in both solutions and aggregates via conjugation-induced rigidity in twisting molecules.<sup>23</sup>

Maleimides, a class of organic fluorophores with many interesting properties such as tunable emission wavelength,<sup>24</sup> sensitivity to solvent polarity,<sup>24,25</sup> high selective reactivity to thiol,<sup>26,27</sup> have been used as OLED materials,<sup>28,29</sup> metal ion sensors,<sup>30,31</sup> pH sensor,<sup>32</sup> cell imaging dyes,<sup>26,27,33</sup> etc. Recently, 2-arylamino-*N*-arylmaleimides have been found to have AIE characteristics<sup>32,34</sup> and mechanochromic luminescence.<sup>35</sup>

 All reported maleimides contain aromatic moieties except two alkylaminomaleimides and four alkylaminobromomaleimides reported in 2015 by O'Reilly group.<sup>36</sup> However, they only studied the optical properties of these aminomaleimids (AMIs) in different solutions.

In our previous research on the multi-component reactions (MCR) of but-2-ynedioate, primary amine, aldehyde for the synthesis of hetereocycles,<sup>37,38</sup> we obtained a byproduct 2-butylamino-*N*-butylmaleimide (**2But** in Scheme 3), whose bright cyan light on thin-layer chromatography plate under daylight, like a fluorescent stick, impressed us deeply. However, we did not pay any attention to the optical properties but the synthetic methodology<sup>37-39</sup> until we developed a convenient five-component reaction for the synthesis of a series of novel C6-unsubstituted tetrahydropyrimidines (THPs) with useful AIE characteristics.<sup>40</sup> Interestingly, we found that THPs possess unconventional intramolecular through-space electronic conjugation<sup>22</sup> and can be used as fluorescent sensors for copper ion,<sup>41</sup> the critical micelle concentration (CMC) of ionic surfactants<sup>42,43</sup> and temperature.<sup>44</sup> In the process of the investigation into the application of THPs as fluorescent sensors, we found that although AIE THPs possess the advantage of highly sensitive fluorescence-on-off change, it is difficult to prepare samples for optical measurements because they are used as suspensions<sup>41-43</sup> or solid states<sup>44</sup> whose sizes influence sample stabilities<sup>41-43</sup> or optical properties<sup>44</sup> and hence are needed to be controlled with suitable methods, which increase experimental procedures and difficulties. At this point, an assumption came upon to our mind that if a fluorophore can be used as fluorescence-on-off sensor in solution, it will be advantageous both in the high sensitivity of fluorescence-on-off change and in the convenience and simplicity of sample preparation. The simple molecular structure and strong solid-state fluorescence of 2But excited our interest so that we raised the questions: Can 2But be used as a fluorescence-on-off sensor in solution? Does it show AIE, ACQ or high emission in both monomers and aggregates? What is the influence of substituents on the optical properties of AMIs? To answer these questions, we synthesized aminomaleimides (AMIs) with aryl and alkyl substituents and studied their optical properties in different solvents and powders via steady-state absorption, excitation and emission spectra as well as fluorescence quantum yields ( $\Phi_F$ ).

Here, the results are reported.

#### **RESULTS AND DISCUSSION**

#### **Design and synthesis**

AMIs can generally be synthesized from 3-halofuran-2,5-dione (1) via route  $1^{45,46}$  or from dimethyl but-2-ynedioate (2) via route II,<sup>34,47,50</sup> (Scheme 1). Route I contains a two-step<sup>46</sup> and a three-step reactions<sup>45</sup> that can afford both various mono-substituted-aminomaleimides (MAMIs) and disubstituted-aminomaleimides (DAMIs). However, the two-step<sup>46</sup> and three-step reaction<sup>45</sup> in route I can afford only 8-35% of total yields. Route II includes a two-step reaction. In our previous work,<sup>38</sup> we studied the influence of solvents on the reaction of 2 and primary amines (R<sup>1</sup>NH<sub>2</sub>) and found that protic and aprotic solvents, respectively, favour the formation of *cis*- and *trans*-enamines, but only a mixture of *cis*- and *trans*-enamines (*cis/trans*=97:3) was obtained because they were inter-convertible during processes of separation and purification. The reaction of 2 and R<sup>1</sup>NH<sub>2</sub> (R<sup>1</sup> = alkyl or aryl without strong electron-withdrawing groups such as NO<sub>2</sub>-), acting as an exothermic reaction, can be conducted at room temperature in different solvents in yields higher than 98%. The two-step reactions in route II can proceed in one-pot still with good to excellent yields.<sup>34,47,48,50,51</sup> The one-pot reaction can proceed successfully at room temperature when R<sup>2</sup> is alkyl,<sup>50,51</sup> but can do only at temperature higher than 180 °C when R<sup>2</sup> is aryl without

electron-withdrawing groups and R<sup>1</sup> are aryl.<sup>34,47,48</sup> The synthesis of MAMIs with  $R^1-R^2 = alkyl-aryl and DAMIs via$ the one-pot reaction has not been reported. In this study, we tried the synthesis under different conditions, but failed. Then, we optimized solvents and temperature, and found that both MAMIs and DAMIs could be synthesized by the one-pot three-component reaction (3CR) in good yields (method I depicted in Scheme 2). With the highly efficient 3CR in hand, we synthesized MAMIs with R<sup>2</sup>=aryl and DAMIs via the 3CR in Scheme 2 and MAMIs with R<sup>1</sup>=alkyl

via the reported 3CR<sup>51</sup> in Scheme 3.



Scheme 1 Two conventional routes for the synthesis of MAMIs and DAMIs



Scheme 2 Synthesis of DAMIs or MAMIs with R<sup>2</sup>=aryl via the developed 3CR in this work



Scheme 3 Synthesis of MAMIs with R<sup>2</sup>=alkyl via the reported 3CR<sup>51</sup>

#### Optical properties of 2But in different solvents and aggregate sizes

The optical properties of **2But** in different solvents were investigated firstly. As depicted in Figure 1, **2But** shows an obvious red shift in absorption ( $\lambda_{ab}$ ) (39 nm) (Figure 1b) and emission peaks ( $\lambda_{em}$ ) (85 nm) (Figure 1a and 1c) from nonpolar cyclohexane (CH) to polar water. Meantime, the fluorescence was quenched in water. The detailed optical data of **2But** are listed in Table 1. Compared with the optical data of **2But** in CH, polar aprotic solvents THF and MeCN displayed small influence on  $\lambda_{ab}$  (red-shift of 12 and 20 nm, respectively) and  $\Phi_F$  (1.2 and 1.6 times lower, respectively), and almost no influence on Stokes shift ( $\Delta$ s) (red-shift of only 4 and 5 nm, respectively). However, protic solvents ethanol (EtOH) and water caused sharp decrease of  $\Phi_F$  (23 and 700 times lower, respectively), distinct red-shift of  $\lambda_{ab}$  (23 and 39 nm, respectively) and changes in  $\Delta$ s (30 and 46 nm, respectively). The fluorescence quenching as well as the large changes in  $\lambda_{ab}$  and  $\Delta$ s are expected to be caused by hydrogen bonding between protic solvent and **2But** as reported many fluorophores containing carbonyl group.<sup>52-55</sup>



Figure 1 Optical properties of 2But in cyclohexane (CH), tetrahydrofuran (THF), acetonitrile (MeCN), ethanol (EtOH) and water (H<sub>2</sub>O) ( $2.00 \times 10^{-5}$  M). (a) 2But in different solvents under daylight (upper) and UV light (365 nm) (lower), (b) Absorption spectra and (c) Emission spectra (excited at peak marked in Figure 1b, excitation and emission slit widths: 3 and 3 nm).

Table 1 Optical properties of 2But in solutions and aggregates.

Solution or	ε <sup>a</sup>	$\lambda_{ab}$	$\lambda_{ m em}$	Δs	${\pmb \Phi_{\rm F}}^{ m b}$
aggregate	$/cm^{-1} M^{-1}$	/nm	/nm	/nm(cm <sup>-1</sup> )	/%
СН	4165	345	445	100(6514)	70
THF	3915	357	461	104(6319)	62/63 <sup>c</sup>
MeCN	4040	365	470	105(6121)	44

EtOH	5955	368	498	130(7094)	3
H <sub>2</sub> O	3220	384	530	146(7174)	0.1
Crystal-L		426 <sup><i>d</i></sup>	480	54 (2641)	50 <sup>c</sup>
Crystal-S		395 <sup>d</sup>	476	81(4308)	56 <sup>c</sup>
Powder		380 <sup><i>d</i></sup>	472	92(5129)	69 <sup>c</sup>

<sup>*a*</sup> Molar absorption coefficient of **2But** in solution ( $2.00 \times 10^{-5}$  M). <sup>*b*</sup> Relative quantum yields with 9,10-diphenylanthracence (DPA) in ethanol ( $5.00 \times 10^{-6}$  M) as standard ( $\Phi_{\rm F}$ =0.95)<sup>56</sup> (excited at 350 nm). <sup>*c*</sup>Absolute quantum yield determined via calibrated integrating sphere (excited at 350 nm). <sup>*d*</sup> Energy-lower excitation peak in Figure 2b.

The optical properties of **2But** in solids were investigated to understand the influence of aggregation on its optical properties. Since the fluorescence efficiencies of conventional organic fluorophores correlate with aggregate sizes, <sup>57,61</sup> the  $\Phi_{\rm F}$  values of **2But** in different aggregate sizes were measured. As shown in Figure 2, when aggregate size decreases from large crystal to powder (ground crystals) (Figure 2a), **2But** shows a blue shift of 47 nm in  $\lambda_{\rm em}$  (left spectra in Figure 2b) but a blue shift of only 8 nm in  $\lambda_{\rm em}$  (right spectra in Figure 2b). Meanwhile, the  $\Phi_{\rm F}$  increases from 50 to 69 % (Table 1). The fluorescence quantum yield (69%) of **2But** in powder is almost the same as that (70%) in CH, that is, the fluorescence efficiencies of **2But** in aggregate sizes is because Coulombic interaction energies between molecules become smaller, resulting in the wider band gaps. <sup>58,62,63</sup> The slight changes in the  $\lambda_{\rm em}$  and  $\Phi_{\rm F}$  with aggregate size might mainly arise from the reabsorption of energy-higher fluorescence<sup>64</sup> because the Stokes shift (53 nm) of **2But** in crystals is much smaller than that (92 nm) in powder.



**Figure 2** Optical properties of **2But** in different sizes of aggregates. (a) photos taken under daylight (upper) and UV light (365 nm) (lower), (b) excitation (left) and emission (right) spectra. L and S stand for large and small, respectively.

#### Optical properties of other AMIs in different solvents and powder

**2But** possesses high emission in both monomers and aggregates, and its high emission is quenched in protic solvents. What about the optical properties of other AMIs with aliphatic or aromatic substituents? To answer this question, we designed and synthesized other 11 AMIs (molecular structures are shown in Scheme 2 and 3). The optical properties of all synthesized AMIs in different solvents and powder are listed in Table 2. It can be seen that substituents show great influences on the  $\Phi_F$  values of AMIs in different solvents. According the substituent influence on  $\Phi_F$ , AMIs can be classified into three types: dialkyl MAMIs (entries 1–7), trialkyl DAMIs (entry 8) and aryl AMIs (entries 9–12). The fluorescence efficiencies of dialkyl MAMIs are highin nonpolar solvent CH ( $\Phi_F = 64-72\%$ ), moderate in polar solvents THF and MeCN ( $\Phi_F = 34-69\%$ ) and very low in protic solvents EtOH and Water (3–0.03%). They have almost the same  $\lambda_{ab}$  and  $\lambda_{em}$  values in CH, which proves that their emissions arise from the same aminomaleimide skeleton. However, only **201** and **2But** are highly emissive in powder ( $\Phi_F = 62$  and 69%), and other dialkyl MAMIs display much lower fluorescence efficiencies ( $\Phi_F = 18-34\%$ ). In other word, only MAMIs with

long chain alkyl demonstrate high emission in both monomers and aggregates, and other dialkyl MAMIs show ACQ

effect.

	Entry	AMIs	Solution /powder <sup>a</sup>	$\epsilon^{b}\!/\!cm^{-1}\!\cdot\!M^{-1}$	$\lambda_{ab}/nm$	$\lambda_{\rm em}/{\rm nm}$	${oldsymbol{\Phi}_{ extsf{F}}}^{c}$ /%
	1	2But	СН	4165	345	445	70
			THF	3915	357	461	62
			MeCN	4040	365	470	44
			EtOH	5955	368	498	3
			Water	3220	384	530	0.1
			powder		380 <sup>d</sup>	472	69 <sup>e</sup>
	2	201	СН	5655	346	446	72
			THF	7100	357	464	53
			MeCN	7040	359	472	36
			EtOH	9675	365	499	2
			Water <sup>f</sup>	1950	362	491	3
			powder		440 <sup>d</sup>	485	62 <sup>e</sup>
	3	2Me	СН	5305	343	448	65
			THF	7850	356	462	45
			MeCN	7660	357	473	26
			EtOH	7805	361	496	2
			Water	7490	374	529	0.1
			powder		437 <sup>d</sup>	483	34 <sup>e</sup>
	4	Cyc-But	СН	3860	345	445	71
			THF	6100	358	463	48
			MeCN	5545	363	472	34
_			EtOH	6105	367	500	2
_							

-	- -	Water	2575	379	535	0.03
		powder		440 <sup>d</sup>	486	34 <sup>e</sup>
5	<b>But-Phc</b>	СН	3150	344	448	71
		THF	3850	357	463	69
		MeCN	4775	358	470	40
		EtOH	4895	361	495	5.4
		Water	2460	381	526	0.3
		powder		434 <sup>d</sup>	486	31 <sup>e</sup>
6	Phc-But	СН	3040	344	446	70
		THF	3640	357	460	63
		MeCN	3285	359	473	43
		EtOH	4435	364	496	5.0
		Water	1680	380	527	0.3
		powder		433 <sup>d</sup>	488	18 <sup>e</sup>
7	Phc-Me	СН	3040	344	446	66
		THF	2910	357	461	45
		MeCN	3200	360	470	43
		EtOH	4525	367	497	0.1
		Water	4785	377	527	0.0
		powder		438	486	21 <sup>e</sup>
8	Pid-Phc	СН	2315	370	464	88
		THF	2465	380	476	7
		MeCN	6705	382	490	1
		EtOH	5620	388	516	1
		Water	3680	405	547	0.3
		powder		464 <sup>d</sup>	506	25 <sup>e</sup>
9	2Ph	СН	3505	370	447	0.3
		THF	3065	379	435	0.9
		MeCN	4690	380	ne	ne
		EtOH	3085	382	ne	ne
		powder		449 <sup>d</sup>	496	17 <sup>e</sup>
10	Ph-But	СН	7235	366	450	8.6
		THF	6670	375	454	0.0
		MeCN	6535	378	ne	ne

60

	-	EtOH	8075	384	ne	ne
		powder		440 <sup><i>d</i></sup>	492	39 <sup>e</sup>
11	But-Ph	СН	2035	352	452	2
		THF	2505	363	473	0.5
		MeCN	3400	367	460	0.3
		EtOH	4575	372	ne	ne
		powder		414 <sup><i>d</i></sup>	474	38 <sup>e</sup>
12	Pid-Ph	СН	4335	371	486	0.7
		THF	4365	378	491	1
		MeCN	5055	382	495	0.9
		EtOH	4425	390	520	0.6
		powder			ne	ne

<sup>*a*</sup>Ground crystals or as-prepared solid. <sup>*b*</sup>Molar absorption coefficient of AMIs in solution ( $2.00 \times 10^{-5}$  M). <sup>*c*</sup>Relative quantum yields with 9,10-diphenylanthracence (DPA) in ethanol ( $5.00 \times 10^{-5}$  M) as standard ( $\Phi_F = 0.95$ )<sup>56</sup> (excited at 350 nm). <sup>*d*</sup>Energy-lower peak in excitation spectrum. <sup>*e*</sup>Absolute quantum yield determined via calibrated integrating sphere (excited at 350 nm). <sup>*f*</sup> **201** is not completely soluble in water. ne: no emission.

Alkyl DAMI **Pid-Phc** (entry 8) is highly emissive ( $\Phi_{\rm F}$ =88%) in CH but almost no emissive in aprotic polar and protic solvents. Compared with dialkyl MAMI **But-Phc** in CH (entry 5), **Pid-Phc** shows 26 nm of red shift in  $\lambda_{ab}$  and 18% increase in  $\Phi_{\rm F}$ , which means that the substitution of hydrogen on N by alkyl increases the electron conjugation and hence leads to a red shift in  $\lambda_{ab}$  and enhancement in  $\Phi_{\rm F}$ . In addition, the emission of **Pid-Phc** is quenched not only by protic solvents but also by polar aprotic solvents. The moiety "-N-C=C-C=O" in AMIs, a typical electron donor and acceptor structure, usually takes place twisted intramolecular charge transfer (TICT) and leads to fluorescence quenching in polar solvent.<sup>65-68</sup> Therefore, the fluorescence quenching of **Pid-Phc** in polar solvents is expected to be caused by TICT. The reason why the fluorescence of alkyl MAMIs is not quenched in polar solvent

might be that the intramolecular hydrogen bond (HB) between hydrogen on N and adjacent carbonyl oxygen prevents the rotation of C-N bond in -N-C=C-C=O moiety, that is, prevents the TICT effect. Although the  $\Phi_{\rm F}$  of **Pid-Phc** is high to 88% in CH, its  $\Phi_{\rm F}$  in powders is only 21%, which means that it displays stronger ACQ effect.

Aryl AMIs (entries 9–12) display very weak or almost no emission in different solvents owing to nonradiative transition that is caused by phenyl rotation as common AIE compounds with aromatic rotors.<sup>9,20,22</sup> Compared with **2But** in CH (entry 1), **Ph-But** (entry 10) and **But-Ph** (entry 11) show 21 and 7 nm of red shifts in  $\lambda_{ab}$ , respectively, which indicates that phenyl at different positions could enhance the electron conjugation to varied extents. The  $\Phi_F$  values of aryl MAMIs **2Ph**, **Ph-But** and **But-Ph** in powder are 17, 39 and 38%, respectively, and aryl **DAMI** is not emissive (entry 12). That is, aryl MAMIs show AIE effect and aryl DAMI is not emissive in both monomers and aggregates.

#### Single-crystal structures of alkyl and aryl AMIs

The excitation peaks of AMIs in powders are distinctly red-shifted (35–105 nm of red shift) compared with their  $\lambda_{ab}$  values in CH (Table 2), which indicates the red-shifted emissions in powder originate from aggregates rather than molecular planarization.<sup>69</sup> The formations of dimers,<sup>70</sup> excimers,<sup>71-73</sup> short-range ring interactions<sup>22</sup> and J-aggregate (aggregate that molecules are arranged in head-to-tail)<sup>5,74,75</sup> usually cause such red shifted emissions in aggregates. To understand the red-shifted emission of AMIs in aggregates, the single crystal structures of alkyl MAMIs (**2But**, **Cyc-But** and **Phc-Me**) and DAMI (**Pid-Phc**), aryl MAMI **Ph** as well as aryl/alkyl MAMI **Ph-But** were investigated. (All single crystal structures are measured in this work except that of **Ph**,<sup>34</sup> and the main crystallographic data of these AMIs are shown in Table S1 in the Supporting Information.).

From the molecular packing on bc plane shown in Figure 3a–d, it can be seen that the molecules of dialkyl MAMIs (2But, Cyc-But and Phc-Me) and aryl/alkyl MAMI Ph-But are connected as dimers via two N-H...O  $(2.08-2.28 \text{ Å}, 160-169^\circ)$  HBs (marked as green a) and the dimers are connected by two weaker C-H...O (2.47-2.54 Å, 142–177°) (market as green b). Weak intramolecular HBs could be observed (marked as green c and d). The dimers are packed as two parallel stairs with central ring coplane and the nitrogen atom of central ring on opposite site (DS1 and DS2 represent two parallel stairs packed via dimers). Although all these MAMIs show similar dimer-packed parallel stairs, the short-range ring interactions with the distance (r) between ring centres shorter than 5 Å are different. The short-range ring interactions between stairs exist in all these MAMIs, but the interactions along stair direction are observed only in **2But**. Compared with the  $\lambda_{ab}$  (345 and 344 nm, respectively) and  $\Phi_{\rm F}$  (71 and 70%, respectively) values of Cyc-But and Phc-Me in CH, 2But in CH has almost the same  $\lambda_{ab}$  (345 nm) and  $\Phi_F$  (70%) values. However, 2But in powders are obviously different from Cyc-But and Phc-Me in powders in terms of the values of  $\lambda_{ex}$  (380 nm vs. 440 and 433 nm, respectively) and  $\Phi_{F}$  (69% vs. 34 and 18%, respectively). Since they have almost the same optical properties in monomers and similar molecular packing modes (dimer-packed parallel stairs), the distinctly different optical properties between them are assumed to come from the different intermolecular interactions along stair direction.



Figure 3 Molecular alignments of 2But (CCDC 1430703), Cyc-But (CCDC 1513071), Phc-Me (CCDC

1513072), **Ph-But** (CCDC 1513073), **Ph** (CCDC 938824)<sup>34</sup> and **Pid-Phc** (CCDC 1430704) in single crystals. (a) –(e) front view (upper) and side view (lower). Hydrogen atoms in the side view were omitted for clarity. The molecules in Figure 3e are marked in different colours for clarity and indication of different molecular conformations.

The molecular arrangement on *bc* plane of diaryl MAMI **2Ph** (upper in Figure 3e) is different from those of dialkyl or alky/aryl MAMIs. The molecules on *bc* plane are connected as layers rather than dimers via intermolecular N-H...O and C-H...O. Since four different conformations exist in single crystals, the two kinds of intermolecular HBs are different in different layers (N-H...O in layer 1 and 2: 2.12 Å, 162° and 2.13 Å, 159°, marked as  $a_1$  and  $a_2$ , respectively; C-H...O in layer 1 and 2: 2.42 Å, 130° and 2.43 Å, 132°, marked as  $b_1$  and  $b_2$ ). From side view (lower in Figure 3e), it can be seen that the molecules are paced as zigzag lines (ZLs) via short-range ring interactions between the central rings with *r*=4.08 and 4.03 Å. The dihedral angle between the central rings along the zigzag lines is equal to 18° with the nitrogen atom of central ring on opposite site. In addition, there are five weak C-H... $\pi$  bonds (2.64–2.97 Å, 132–144°) between the adjacent molecules. All molecules of **2Ph** in aggregates are connected as a net by intermolecular HBs and short-range ring interactions. Since the distance *r* along zigzag lines is near 4 Å, which means the existence of strong  $\pi$ - $\pi$  interactions, the large red-shift emission of **2Ph** is expected to originate mainly from the zigzag line arrangement.

The molecular packing of DAMI **Pid-Phc** is shown in Figure 3f. Without hydrogen on N atom, that is, without intermolecular N-H...O, the distance *r* between the central rings becomes shorter (3.87 Å) and forms slipped parallel dimmers,<sup>76,77</sup> which will lead to excimer formation and hence fluorescence decrease or quenching.<sup>1</sup> This explains distinct fluorescence decrease of **Pid-Phc** in powder ( $\Phi_F$ =25%) compared to that in CH ( $\Phi_F$ =88%) and the almost

noemssion of **Pid-Ph** in powder.

The single crystal structures of these AMIs indicate that intermolecular N-H...O and  $\pi$ - $\pi$  stacking interaction are two important factors influencing molecular packing of AMIs. For dialkyl or aryl/alkyl MAMIs, the intermolecular hydrogen bond N-H...O is the main factor, which leads to formation of hydrogen-bonded dimmers that are packed as parallel stairs with *r*>4.56 Å; for diaryl MAMIs, intermolecular  $\pi$ - $\pi$  stacking interaction becomes the main factor, which leads to  $\pi$ - $\pi$ -packed zigzag arrangement with r = 4.03 and 4.08 Å; and for DAMIs without hydrogen on nitrogen atom, that is, without intermolecular N-H...O,  $\pi$ - $\pi$  stacking interaction leads to the formation of  $\pi$ - $\pi$ -packed slipped parallel dimers with r = 3.87 Å. These molecular packing modes and the *r* values show great influence on the fluorescence efficiencies of AMIs. Only the parallel stair-like arrangement packed via hydrogen-bonded dimers with r = 4.931 Å in **2But** gives high solid-state emission.

#### CONCLUSION

In this study, we have investigated into the synthesis and structure-property-relationship of AMIs. A 3CR based on 3-halofuran-2,5-dione (method I) has been developed for the synthesis of DAMIs and MAMIs with different substituents in the overall yields (75–85%) much higher than those (8–35%) of the reported two-step or three-step reactions in route I. In addition, we found that the reported 3CR based on dimethyl but-2-ynioaedte (method II) is suitable for the synthesis of *N*-alky MAMIs but limited to the synthesis of DAMIs and *N*-aryl MAMIs. Furthermore, 12 AMIs were designed and synthesized for investigation of the relationship between structures and optical properties. Our experimental results indicate that the fluorescence efficiencies of AMIs in monomers and aggregates can be easily tuned by switch of alkyl and aryl: Alkyl AMIs show high emission in both monomers and aggregates or ACQ

effect, while aryl and aryl-alkyl AMIs display almost no emission in both monomers and aggregates or AIE effect.

The high emissions ( $\Phi_{\rm F}$  up to 88%) of AMIs in monomers, proving to originate from aminomaleimide skeleton, will be quenched in protic solvents by hydrogen bonding effect for alkyl MAMIs, in polar solvents by TICT effect for alkyl DMIs, or in different solvents by the rotations of aryl for aryl and aryl/alkyl AMIs. The red-shifted emissions of AMIs in aggregates as compared to those in monomers mainly correlate with intermolecular N-H...O and  $\pi$ - $\pi$ stacking interactions that cause formation of dimer-packed parallel stair-like arrangements, zigzag lines or  $\pi$ - $\pi$ -stacked dimers. The simple synthesis method, high emission in both monomers and aggregates, and sensitive response to protic and polar solvents of AMIs are useful for practical applications. The further investigation into the applications of AMIs as bio- and chemical fluorescent sensors are underway in our laboratory.

#### **EXPERIMENTAL SECTION**

#### **Materials and Instruments**

All the chemicals used in this study were obtained from commercial suppliers and used without further purification. For measurement of the optical spectra of samples, spectroscopically pure solvents and doubly distilled water were used. All melting points were taken on amicro melting point apparatus and are uncorrected. <sup>1</sup>H NMR (400 MHz) and <sup>13</sup>C NMR (100.6 MHz) spectra were recorded on a 400 MHz NMR spectrometer using CDCl<sub>3</sub> as solvent and TMS as internal standard. Low resolution and high resolution mass spectra were obtained using electrospray ionization (ESI) and quadrupole-linear ion-trap techniques. IR spectra were obtained as liquid films on potassium bromide pellets with a Fourier transform-infrared spectroscopy. Photos were taken by Canon PC1356. The absorption as well as the fluorescence excitation and emission properties were analyzed by an UV-Vis spectrophotometer

(measurement wavelength range: 190–100 nm; wavelength accuracy:  $\pm 2$  nm) and a spectrofluorophotometer (150 W Xenon lamp; measurement wavelength range: 220–750 nm; wavelength accuracy:  $\pm 1.5$  nm; S/N ratio:150; slit width: 1.5/3/5/10/15/20), respectively. The absolute fluorescence quantum yields were measured using calibrated integrating sphere.

#### General procedure for the one-pot synthesis of *N*-alky1 MAMIs (entries 1-7 and 10 in Table 2)

The intermediate enamines were prepared by the addition reaction of dimethyl but-2-ynedioate and primary amine as described in our previous work.<sup>38</sup> That is, the mixture of EtOH (6 mL), dimethyl but-2-ynedioate (284 mg, 2 mmol) and primary (2 mmol) were kept at room temperature for 5–10 min for the synthesis of intermediate enamines. Then, to the reaction mixture, primary aliphatic amine (8 mmol) was added. After the reaction was completed (stirred at room temperature for 48 h), the product mixtures were purified by column chromatography with petroleum ether-ethyl acetate (6:1) as eluent to afford the desired products (60–88% yields).

#### General procedure for the one-pot synthesis of N-aryl MAMIs (entries 9 and 11 in Table 2) and DAMIs

#### (entries 8 and 12 in Table 2)

Bromomaleic anhydride (389 mg, 2.2 mmol) and primary amine (2 mmol) were added into 4 mL of tolurene in sequence, kept at rt for 10 min and then at 110 °C for 6 h. Then, to the reaction mixture, primary or secondary amine (3 mmol) was added. The reaction mixture was stirred until the temperature was reduced to room temperature, and then the solution was removed by compressed air. Then crude product was separated by column chromatography with petroleum ether-ethyl acetate (6:1) as eluent to afford the desired products (75–85% yield).

Preparation of 2But in different aggregate sizes

Different sizes of crystals of **2But** were prepared by recrystallization from dichloromethane/*n*-hexance solution at room temperature for different time.

#### Preparation of AMIs in different solvents (2.00×10<sup>-5</sup> M)

Tetrahydrofuran stock solutions of 12 aminomaleimides (AMIs) with a concentration of 1 mM were prepared, respectively. 100  $\mu$ L of the stock solution was then transferred to 5 mL volumetric flasks, with tetrahydrofuran removed by N<sub>2</sub> and then the flasks filled to the mark with corresponding solvents for preparation of different solutions of **12** AMIs except their tetrahydrofuran solutions. The tetrahydrofuran solutions of **12** AMIs were prepared by adding 100  $\mu$ L of tetrahydrofuran stock solutions into 5 mL volumetric flask, and then filling the flasks to the mark with tetrahydrofuran.

Structure Characteristics of 12 AMIs in Table 2

**2-butylamino-***N***-butylmaleimide (2But)**: 78% (350 mg, 1.56 mmol) yield, light yellow solid, mp= 81.0–81.3°C; IR (KBr):  $v_{max}$  = 3321, 3097, 2955, 2933, 2866, 1689, 1636, 1448, 1035, 783 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.34 (s, 1H), 4.80 (s, 1H), 3.48 (t, *J* = 7.2 Hz, 2H), 3.21–3.16 (m, 2H), 1.71–1.52 (m, 4H), 1.49–1.28 (m, 4H), 0.98 (t, *J* = 7.2 Hz, 3H); 0.94 (t, *J* = 7.6 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.6, 167.6, 149.2, 83.7, 43.9, 37.3, 30.8, 30.5, 20.0, 13.6 ppm; MS (ESI): *m*/z 225 (M+H<sup>+</sup>, 100), 449 (2M+H<sup>+</sup>, 95) and HR-ESI-MS for C<sub>12</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub> ([M+Na]<sup>+</sup>) Calcd: 247.1417; Found: 247.1414. The compound has CAS Registry Number (457959-70-5) but no reference on it has been found by SciFinder.

**2-oleylamino-***N***-oleylmaleimide (201)**: 69% (845 mg, 1.38 mmol) yield, yellow solid, mp=62.5–62.6°C; IR (KBr):  $v_{\text{max}} = 3477, 3334, 2955, 2915, 2849, 1692, 1643, 1469, 1099, 1266, 742 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)$ 

  $\delta = 5.37-5.33$  (m, 4H), 4.76 (s, 1H), 3.43 (t, J = 7.2 Hz, 2H), 3.14 (q, J = 6.8 Hz, 2H), 2.00 (s, 5H), 1.63–1.53 (m, 6H), 1.25 (s, 47H), 0.89–0.85 (t, J = 6.4 Hz, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 172.6$ , 167.6, 149.2, 123.0, 129.9, 83.7, 44.3, 37.6, 32.5, 31.9, 29.3, 27.2, 26.8, 22.6, 14.1 ppm; MS (ESI): m/z 635 (M+H<sup>+</sup>, 10), 301 (100) and HR-ESI-MS for C<sub>40</sub>H<sub>72</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 613.5667; Found: 613.5654.

**2-methylamino-***N***-methylmaleimide** (**2Me**): 60% (168 mg, 1.2 mmol) yield, yellow solid, mp = 147.2–147.4°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.43 (s, 1H), 4.84 (s, 1H), 2.98 (s, 1H), 2.95 (d, *J*=5.6 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.5, 167.4, 150.4, 84.1, 30.5, 23.4 ppm; <sup>1</sup>H and <sup>13</sup>C NMR spectra are consistent with the previous literature<sup>51</sup>. **2-cyclohexylamino-***N***-butylmaleimide** (**Cyc-But**): 73% (365 mg, 1.46 mmol) yield, light yellow solid, mp= 73.8–74.1°C; IR (KBr):  $v_{max}$  = 3327, 3021, 2930, 2858, 1698, 1633, 1452, 1439, 1379, 1335, 1169, 1108, 1049 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 5.34 (d, *J* = 6.8, 1H), 4.77 (s, 1H), 3.47 (t, *J* = 7.2, 2H), 3.18–3.15 (m, 1H), 2.02–1.99 (m, 2H), 1.82–1.53 (m, 5H), 1.42–1.24 (m, 7H), 0.93 (t, *J* = 7.2, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 172.7, 167.8, 147.9, 83.4, 53.1, 37.3, 31.9, 30.8, 25.3, 24.4, 19.9, 13.6 ppm; MS (ESI): *m/z* 635 (M–H<sup>+</sup>, 30), 75 (100) and HR-ESI-MS for C<sub>14</sub>H<sub>22</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 251.1754; Found: 251.1769.

**2-butylamino-***N***-benzylmaleimide (But-Phc)**: 78% (403 mg, 1.56 mmol) yield, light yellow solid, mp =  $107.2-107.6^{\circ}$ C; IR (KBr):  $v_{max} = 3323$ , 3117, 2923, 1739, 1701, 1617, 1402, 1053, 696, 654 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.38-7.27$  (m, 5H), 5.35 (s, 1H), 4.84 (s, 1H), 4.65 (s, 2H), 3.20–3.15 (m, 2H), 1.67–1.58 (m, 2H), 1.44–1.39 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.3$ , 167.2, 149.3, 136.8, 128.5, 83.9, 44.0, 41.0, 30.5, 19.9, 13.6 ppm; MS (ESI): *m*/z 259 (M+H<sup>+</sup>, 90), 534 (2M+NH<sub>4</sub><sup>+</sup>, 100) and HR-ESI-MS for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 259.1441; Found: 259.1439. The compound has CAS Registry Number (607692-63-7)

but no reference on it has been found by SciFinder.

**2-benzylamino-N-butylmaleimide** (**Phc-But**): 88% (454 mg, 1.76 mmol) yield, yellow solid, mp = 121.3–121.9°C; IR (KBr):  $v_{max}$  = 3332, 3125, 2953, 2862, 1749, 1698, 1620, 1444, 1026, 781, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.42–7.18 (m, 5H), 5.67 (s, 1H), 4.86 (s, 1H), 4.35 (d, *J* = 5.6 Hz, 2H), 3.48 (t, *J* = 7.2 Hz, 2H), 1.61–1.54 (m, 2H), 1.38–1.28 (m, 2H), 0.94 (t, *J* = 7.6 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 172.5, 167.5, 148.8, 135.7, 128.9, 128.2, 127.7, 85.3, 48.4, 37.8, 30.7, 19.9, 13.6 ppm; HR-ESI-MS for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 259.1441; Found: 259.1445. The compound has CAS Registry Number (607692-56-8) but no reference on it has been found by SciFinder.

2-benzylamino-*N*-methylmaleimide (Phc-Me): 72% (311 mg, 1.44 mmol) yield, yellow solid, mp = 151.2–151.3°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.38–7.29 (m, 5H), 5.69 (s, 1H), 4.88 (s, 1H), 4.37(d, J = 5.6 Hz, 2H), 2.99 (s, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 172.4, 167.6, 149.0, 135.6, 129.0, 128.2, 127.6, 85.4, 48.4, 23.4 ppm; <sup>1</sup>H and <sup>13</sup>C NMR spectra are well correspondent to the previous literature.<sup>50</sup>

**2-(piperidin-1-yl)-***N***-benzylmaleimide(Pid-Phc)**: 75% (405 mg, 1.5 mmol) yield, light yellow solid, mp= 107.3–107.8°C; IR (KBr):  $v_{max}$  =2919, 2851, 1701, 1652, 1618, 1540, 1455, 1399, 697, 654 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.45–7.22 (m, 5H), 4.91 (s, 1H), 4.64 (s, 2H), 3.66 (b, 4H), 1.68 (b, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta$  = 170.6, 167.0, 150.4, 137.1, 128.5, 128.3, 127.4, 87.9, 48.4, 40.9, 25.5, 23.9 ppm; MS (ESI): *m*/z 271 (M+H<sup>+</sup>, 50), 558 (2M + NH<sub>4</sub><sup>+</sup>, 100) and HR-ESI-MS for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 271.1441; Found: 271.1435.

**2-phenylamino-***N***-phenylmaleimide (2Ph)**: 85% (449 mg, 1.7 mmol) yield, yellow solid, mp = 245.4–245.8°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.52–7.20 (m, 11H), 5.70 (s, 1H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 171.2,

167.0, 142.4, 138.2, 131.6, 129.8, 129.0, 127.6, 125.8, 124.8, 118.9, 89.1 ppm. <sup>1</sup>H and <sup>13</sup>C NMR spectra are well correspondent to the previous literature.<sup>78</sup>

**2-phenylamino-***N***-butylmaleimide (Ph-But)**: 70% (342 mg, 1.4 mmol) yield, yellow solid, mp = 139.3–139.9°C; IR (KBr):  $v_{max} = 3313$ , 3121, 2956, 2863, 1756, 1686, 1638, 1446, 1421, 1183, 748, 694 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.44-7.16$  (m, 6H), 5.52 (s, 1H), 3.56 (t, J = 7.2 Hz, 3H) 1.66–1.59 (m, 2H), 1.39–1.34 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>):  $\delta = 172.8$ , 168.3, 142.3, 138.4, 129.7, 124.4, 118.7, 88.9, 37.7, 30.7, 20.0, 13.6 ppm; MS (ESI): m/z 245 (M+H<sup>+</sup>, 5), 102 (100) and HR-ESI-MS for C<sub>14</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 245.1285; Found: 245.1299.

**2-butylamino-***N***-phenylmaleimide (But-Ph)**: 78% (381 mg, 1.56 mmol) yield, yellow solid, mp = 138.5–138.8°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  = 7.48–7.32 (m, 5H), 5.53 (s, 1H), 4.99 (s, 1H), 3.26 (q, *J* = 7.2 Hz, 2H), 1.73–1.66 (m, 2H), 1.51–1.42 (m, 2H), 1.00 (t, *J* = 7.2 Hz, 3H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  = 171. 0, 166.3, 149.0, 131.9, 128.9, 127.2, 125.8, 84.2, 44.1, 30.5, 20.0, 13.6 ppm; <sup>1</sup>H and <sup>13</sup>C NMR spectra are well correspondent to the previous literature.<sup>79</sup>

**2-(piperidin-1-yl)-***N***-phenylmaleimide(Pid-Ph)**: 80% (410 mg, 1.6 mmol) yield, light yellow solid, mp = 107.8–108.1°C; IR (KBr):  $v_{\text{max}} = 3101$ , 2923, 2851, 1749, 1697, 1648, 1612, 1448, 1383, 766, 700 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta = 7.47-7.32$  (m, 5H), 5.07 (s, 1H), 3.74 (b, 4H), 1.74 (b, 6H) ppm; <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta = 169.8$ , 166.1, 149.9, 131.9, 128.8, 127.2, 126.4, 88.32, 77.3, 77.2, 76.9, 76.6, 25.6, 23.9 ppm; MS (ESI): *m*/z 279 (M+Na<sup>+</sup>, 40), 102 (100) and HR-ESI-MS for C<sub>15</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) Calcd: 257.1285; Found: 257.1278; <sup>1</sup>H and <sup>13</sup>C NMR spectra are well correspondent to the previous literature.<sup>80</sup>

# ASSOCIATED CONTENT

# \*Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Table S1, <sup>1</sup>H and <sup>13</sup>CNMR spectrum copies of 12 AMIs in Table 2, thermal ellipsoid plots and "cif" files of five

new crystal structures.

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## Notes

The authors declare no competing financial interest.

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