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### Rapid access to $C_3$ - and $C_s$ -symmetric AAT organogelators via ring opening of a common benzotrifuranone precursor

Matthew B. Baker<sup>a</sup>; Ling Yuan<sup>a</sup>; Christopher J. Marth<sup>a</sup>; Yan Li<sup>a</sup>; Ronald K. Castellano<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Florida, Gainesville, FL, USA

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## Rapid access to $C_3$ - and $C_s$ -symmetric AAT organogelators via ring opening of a common benzotrifuranone precursor<sup>†</sup>

Matthew B. Baker, Ling Yuan, Christopher J. Marth, Yan Li and Ronald K. Castellano\*

Department of Chemistry, University of Florida, P.O. Box 117200, Gainesville, FL 32611-7200, USA

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Presented is a rapid and general approach to functionalised 1-aza-adamantanetrione (AAT) donor- $\sigma$ -acceptor molecules from a phloroglucinol-derived trilactone, benzotrifuranone (BTF). Ten  $C_3$ -symmetric AATs bearing diverse aryl amide substituents are accessed in two synthetic steps: (1) the exhaustive ring opening of BTF with aromatic amine nucleophiles (performed in up to 91% yield) and (2) cyclisation with hexamethylenetetramine (performed in up to 75% yield). Additionally, *stepwise ring opening* of BTF allows synthesis of phloroglucinol intermediates with two unique aryl amide substituents and ultimately  $C_s$ -symmetric AATs. Of the novel AATs prepared, three (including the  $C_s$ -symmetric hybrid) are effective gelators of chlorinated solvents (critical gelation concentration (CGC) = 0.2–0.4 wt%) and one, with naphthyl substituents, forms translucent gels from aromatic solvents (CGC  $\sim$  0.3 wt%). The combination of AATs with moderately electron-poor and electron-rich aromatic substituents results in functional complementarity and gelation at concentrations below what is required for the individual components. Electron microscopy of the gel morphologies shows high aspect ratio fibres underlying the gel network superstructures in most cases. Polarised optical microscopy has allowed imaging of representative native organogel phases, and reveals striking morphology differences between gels that also share different optical and/or thermal stability properties.

**Keywords:** donor–acceptor molecules; gels; self-assembly; symmetry; through-bond interactions

### Introduction

1-Aza-adamantanetriones (**1**, **2**) (AATs, Figure 1), with their tricyclic  $\beta$ -aminoketone (**3**) cores, are unique scaffolds that have enabled studies of through-bond (**4**, **5**) (hyperconjugative (**6**–**8**)) interactions at both the molecular (**1**, **9**–**11**) and supramolecular level (**12**, **13**). The rigidity of the core maintains orbital overlap and communication between the donor (amine) and acceptor (carbonyls) through the intervening C–C  $\sigma$ -bonds (D- $\sigma$ -A interactions). Previously shown with alkyl- (R = alkyl) and ester- (R = CH<sub>2</sub>CO<sub>2</sub>R') functionalised AATs, molecular-level consequences of D- $\sigma$ -A interactions include decreased basicity of the bridgehead nitrogen (**9**), bond length alteration as well as the presence of an uncharacteristically strong  $\sigma$ -coupled UV absorption (**1**). Furthermore, as the AAT core bears a significant dipole along its  $C_3$  axis and can be functionalised through organic synthesis, this class of compounds appears attractive for dipole-directed assembly (**14**, **15**) and supramolecular materials construction. Accordingly, several aryl (R = CH<sub>2</sub>Ar) and aryl amide (R = CH<sub>2</sub>CONHAr) derivatives have been shown

to gelate organic solvents (**12**, **13**) at low concentrations (<1 wt%). Complementary theoretical studies have additionally explored the propensity for AATs to self-assemble in a 1-D head-to-tail manner (**16**, **17**) and found that the process is accompanied by a decrease in the HOMO–LUMO gap through the emergence of a unique supramolecular electronic structure.

While computation has implicated assemblies of the AATs as potentially unique low-band gap supramolecular architectures (**16**), rapid access to diversely substituted targets to facilitate requisite structure-assembly studies has remained elusive. The previous synthetic approach to aryl amide functionalised AATs **1**, e.g. involved construction of a protected  $C_3$ -symmetric phloroglucinol substrate **2**, BBr<sub>3</sub> deprotection to afford the phloroglucinol **4** and subsequent cyclisation with hexamethylenetetramine (HMTA) (Figure 2) (**1**, **12**, **13**). Two relatively simple aryl amide AATs have been prepared in this way (**1a** and **1b**, Table 1), (**12**) but the demanding and late-stage deprotection step has limited access to a structurally diverse family of compounds. A straightforward solution is presented here,

\*Corresponding author. Email: castellano@chem.ufl.edu

<sup>†</sup>Dedicated to the memory of Prof. Dmitry M. Rudkevich.

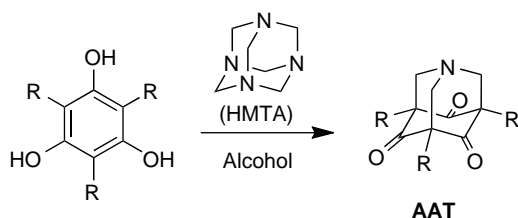


Figure 1. Synthesis of the AAT scaffold from a phloroglucinol precursor.

made possible by the recent development of a phloroglucinol-derived trilactone, benzotrifuranone (BTF) **3** (Figure 2) (18).

First shown is the synthesis of (otherwise inaccessible)  $C_3$ -symmetric phloroglucinol derivatives that are substrates for cyclisation into the corresponding triamide AATs, available in one step through nucleophilic ring opening of BTF's three lactone rings (Figure 2). This synthetic approach allows rapid preparation of AAT targets with increased structural diversity (e.g. bearing electron-rich, electron-deficient and expanded aromatic substituents) and, for the first time, demonstration of how complementary aromatic interactions (19–22) can enhance AAT assembly in the context of mixed gels (23, 24). Second is a BTF-based approach to efficiently prepare the first functionalised AATs of lower ( $C_s$ -) symmetry (i.e. AATs bearing two different types of aryl amide substituents). Desymmetrisation commences with stepwise ring opening of **3** to afford (depending on the reaction conditions) primarily monolactone **5** or dilactone

**6**, chemistry made possible by the 'electronic coupling' of the lactone rings through its aromatic core. Subsequent ring opening with a second aniline ( $H_2NAr^1$ ) and cyclisation affords non- $C_3$ -symmetric AATs capable of displaying hybrid structures and functions.

## Results and discussion

### Synthesis of $C_3$ -symmetric AATs (**3** → **1**)

The general reaction scheme for  $C_3$ -symmetric AAT formation from BTF is shown in Figure 2. BTF (**3**) was synthesised on a multi-gram scale according to recently published methods (18). As shown in Table 1, a variety of electron-rich and -deficient anilines could be used to open the lactone rings of **3**, providing rapid access to phloroglucinol substrates for cyclisation into AATs. As a general procedure, BTF was simply stirred with an excess of nucleophile in an aprotic solvent at temperatures ranging from 60 to 110°C (excess (unreacted) aniline could be recovered through selective extraction and subsequent purification). Anilines in entries **i**, **v**, **vii** and **viii** were able to fully react with **3** in toluene at reflux, with the exhaustively ring-opened species (**4a**, **e**, **g** and **h**, respectively) precipitating from solution as the major product in good yield (30–80%). Although 3,5-dimethoxyaniline is considered a good nucleophile, compound **4d** (entry **iv**) was only formed in appreciable yield after several nights of heating (now in THF at reflux), due to the insolubility of a partially ring-opened (diamide monolactone) intermediate (i.e. **5** in Figure 2). Several other entries (**ii**, **vi** and **x**) required the slightly more polar THF to

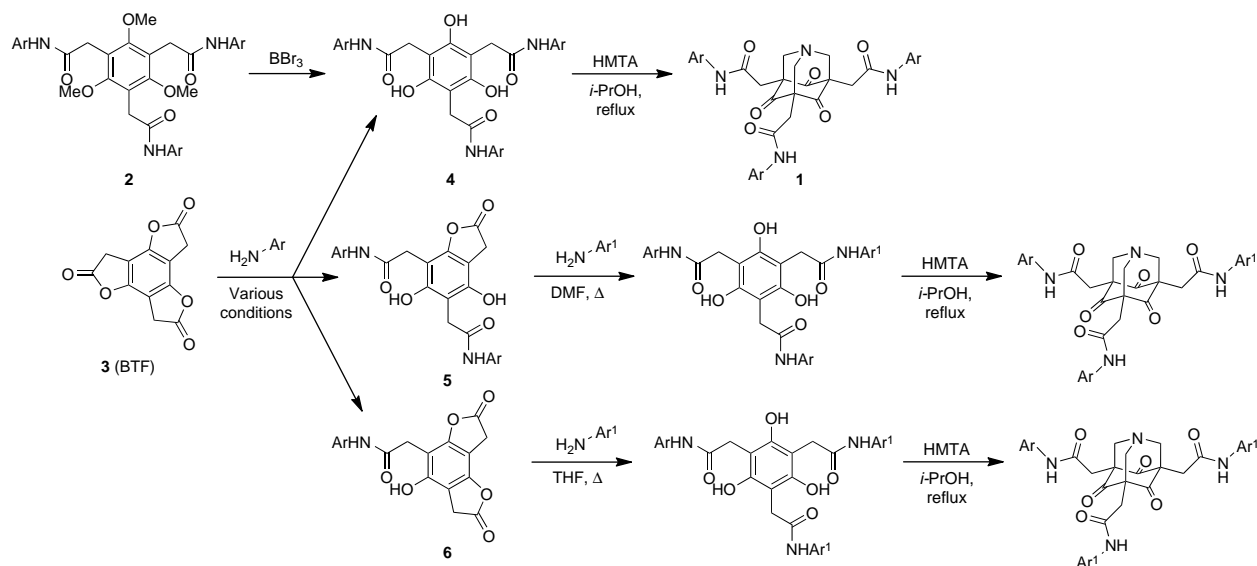
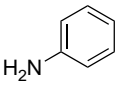
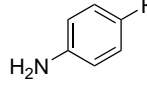
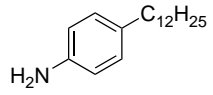
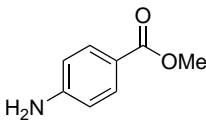
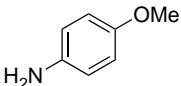
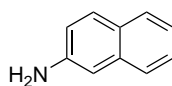
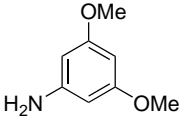
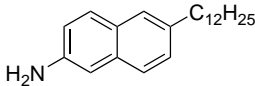
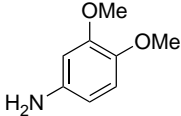
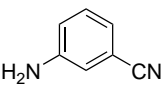
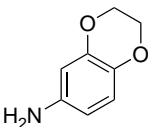
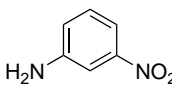


Figure 2. Ring opening of BTF (**3**) to form phloroglucinol derivatives (**4**) provides a much milder route to aryl amide AATs (**1**) than previous (1, 12)  $BBr_3$  deprotection procedures ( $Ar = aryl$ ), and opportunities to rationally prepare non- $C_3$ -symmetric derivatives. HMTA = hexamethylenetetramine.

Table 1. Representative library of  $C_3$ -symmetric AAT derivatives synthesised in two steps from BTF **3**.

Entry	Nucleophile (NH <sub>2</sub> Ar)	Yield ( <b>4</b> )	Yield ( <b>1</b> )	Entry	Nucleophile	Yield ( <b>4</b> )	Yield ( <b>1</b> )
i		78% <sup>a</sup> ( <b>4a</b> )	75% <sup>b</sup> ( <b>1a</b> )	vii		76% <sup>a</sup> ( <b>4g</b> )	35% <sup>b</sup> ( <b>1g</b> )
ii		56% <sup>c</sup> ( <b>4b</b> )	61% <sup>b</sup> ( <b>1b</b> )	viii		68% <sup>a</sup> ( <b>4h</b> )	21% <sup>b</sup> ( <b>1h</b> )
iii		78% <sup>c</sup> ( <b>4c</b> )	53% <sup>b</sup> ( <b>1c</b> )	ix		55% <sup>d</sup> ( <b>4i</b> )	66% <sup>b</sup> ( <b>1i</b> )
iv		42% <sup>c</sup> ( <b>4d</b> )	11% <sup>b</sup> ( <b>1d</b> )	x		25% <sup>c</sup> ( <b>4j</b> )	65% <sup>b</sup> ( <b>1j</b> )
v		33% <sup>a</sup> ( <b>4e</b> )	53% <sup>b</sup> ( <b>1e</b> )	xi		36% <sup>c</sup> ( <b>4k</b> )	– <sup>e</sup>
vi		91% <sup>c</sup> ( <b>4f</b> )	40% <sup>b</sup> ( <b>1f</b> )	xii		40% <sup>c</sup> ( <b>4l</b> )	– <sup>e</sup>

<sup>a</sup> 9 equiv of nucleophile and 1 equiv of BTF in toluene at reflux 16–48 h.

<sup>b</sup> corresponding phloroglucinol substrate and 1.5–3 equiv of HMTA in *i*-PrOH at reflux 16–120 h.

<sup>c</sup> 9 equiv of nucleophile and 1 equiv of BTF in THF at reflux 16–72 h.

<sup>d</sup> 6 equiv of nucleophile and 1 equiv of BTF in DMF 120°C 24 h.

<sup>e</sup> no reaction after 5 days.

realise complete conversion, including anilines featuring more electron-deficient substituents (entries **xi** and **xii**). Phloroglucinols bearing electron-deficient aromatics (**4g**, **h**, **k**, **l**) tended to form fairly insoluble materials, attributed to the increased hydrogen bonding of the amide unit along with the stronger  $\pi$ -stacking interactions expected for the less electron-rich aromatic rings (22, 25). Surprisingly, the use of DMF as a solvent led to incomplete conversion in most cases, and difficulty in the purification of the phloroglucinol targets. It is important to recognise that species **4c–f**, **h**, **k** and **l** were hitherto inaccessible from intermediate **2** (Figure 2).

The phloroglucinol derivatives **4a–j** were then subjected to standard AAT-forming cyclisation conditions (1, 2, 12, 13). As a general procedure, the phloroglucinol substrate was stirred in *i*-PrOH at reflux in the presence of 1.5–3

equivalents of HMTA over 1–5 nights (compounds **4b**, **h**, **i** and **j** needed longer reaction times due to poor solubility of the phloroglucinol); the corresponding insoluble AATs were simply collected by filtration and then washed.

Rapid access to diversely functionalised phloroglucinol substrates from BTF has shed new light on the scope of the AAT-forming cyclisation step (i.e. the conversion of **4** to **1**). While broadly functional group tolerant, at least two classes of phloroglucinols (**4**) do not react well. Those bearing quite electron-deficient aromatics (e.g. **4k** and **4l**) show no evidence (by <sup>1</sup>H NMR analysis) of AAT formation under the standard conditions even over 5 nights. The result is best explained by the significant insolubility (due to the forces identified above) of the substrates. Not implicated is the re-lactonisation of the phloroglucinol substrates under the HMTA cyclisation

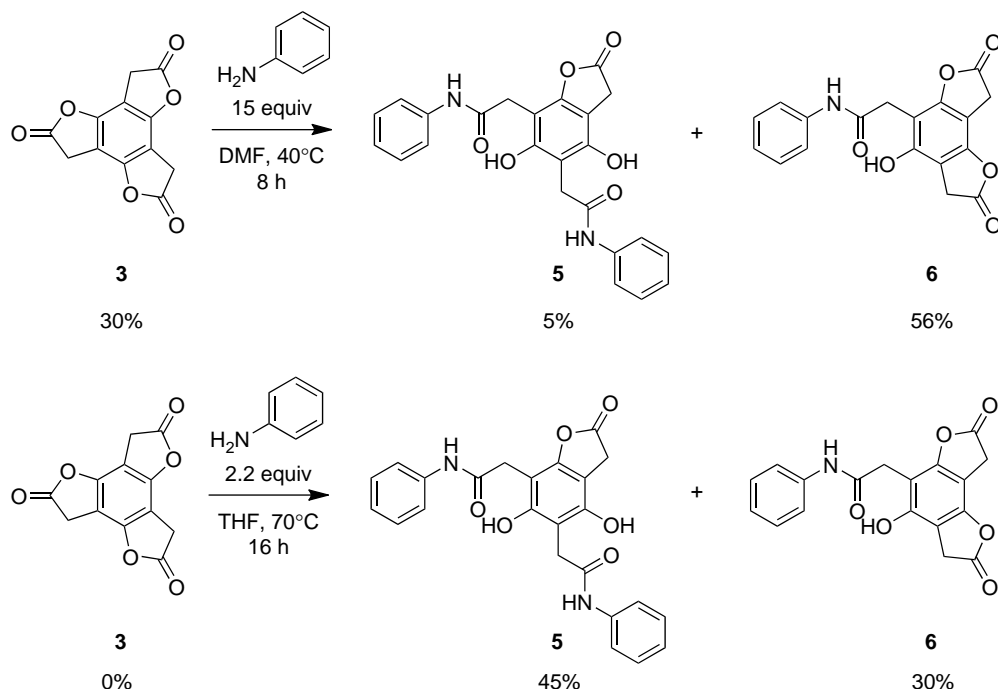


Figure 3. Controlled ring opening of BTF with aniline (yields shown are isolated yields).

conditions, although preliminary evidence does show that this can occur rapidly under acidic conditions (e.g. trifluoroacetic acid/toluene). Also unsuitable for AAT formation are phloroglucinol derivatives with aromatics bearing long alkoxy chains (e.g. OC<sub>12</sub>H<sub>25</sub>, not shown in Table 1). The negative results demonstrate the delicate balance between the solubility of the phloroglucinol starting material and insolubility of the AAT product that dictates cyclisation success. Given that the formation of the AAT core occurs at the expense of phloroglucinol aromaticity, precipitation of the product represents a potential driving force for the reaction. Further investigation into the scope of the HMTA cyclisation is currently underway, aided by the methodology outlined in this manuscript.

### Synthesis of C<sub>s</sub>-symmetric AATs

Differentially functionalised molecular scaffolds can lead to unique hybrid properties and multifunctional materials (26). Traditionally, access to molecules of lower symmetry is realised via a statistical approach from symmetrical precursors (often plagued by low yields and difficult separations), sequential couplings followed by cyclisation (popular in peptides and porphyrins) (27–30) or selective protection/deprotection (generally plagued by low yields and poor atom economy) (31, 32). In rare cases, best characterised by triazine derivatives, (33) the chemical properties of the core allow for desymmetrisation with careful control of reaction conditions.

Alluded to earlier, electronic ‘communication’ between the three lactone rings of BTF **3** via its central aromatic core could be the basis for a controllable stepwise ring opening strategy to form lower-symmetry phloroglucinol derivatives. The nature of the ‘communication’ is presumably largely inductive, but could more subtly involve ring strain and  $\pi$ -conjugation effects that would accompany trace amounts of enol or enolate forms (18). Although the physicochemical details are still very much under investigation, the hypothesis seems plausible given the preliminary results using **3** and aniline (Figure 3). The synthesis of dilactone **6** can be realised in 56% yield (86% based on recovered starting material) using an excess of aniline, mild heating (40°C) and a limited reaction time (8 h). The result demonstrates a relatively rapid initial ring opening of BTF in the presence of nucleophiles. Monolactone **5** could be prepared in good yield (45%) using slightly warmer temperatures and a small excess of aniline.

Both monolactone **5** and dilactone **6** were then used to prepare C<sub>s</sub>-symmetric AAT molecules as shown in Figure 4. Dilactone **6** was opened with an excess of 4-dodecylaniline in hot THF to afford phloroglucinol **4m** that could be isolated by simple filtration; cyclisation of **4m** then led to a 56% yield of AAT **1m**. Correspondingly, monolactone **5** could be ring opened in hot DMF by  $\beta$ -naphthylamine to provide phloroglucinol **4n** in good yield (70%). Subsequent cyclisation with HMTA gave C<sub>s</sub>-symmetric AAT **1n**, one of the two possible hybrid structures of AATs **1a** and **1i**.

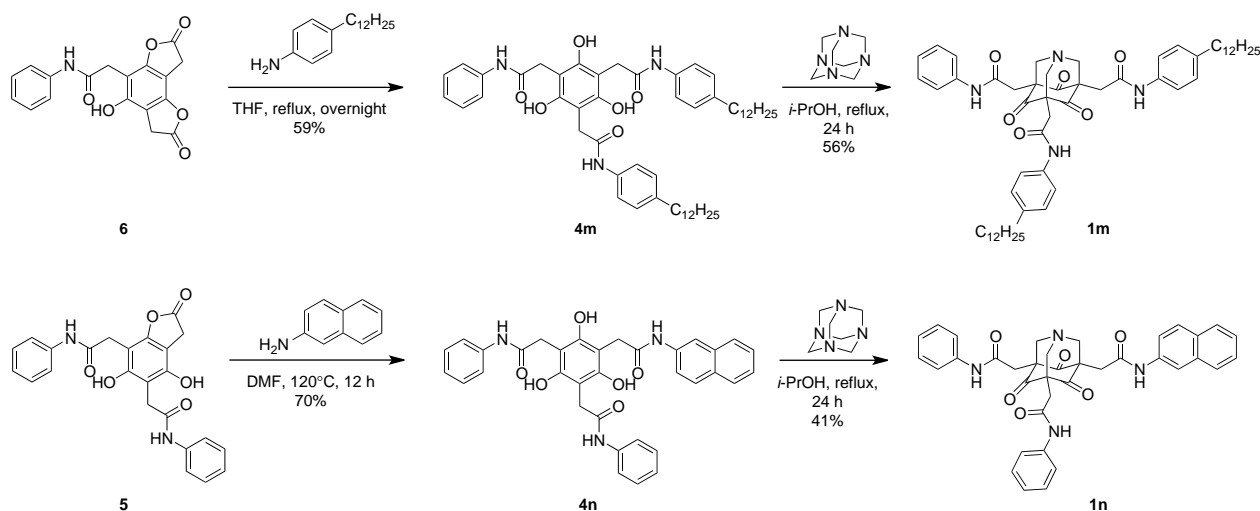


Figure 4. Utilisation of **5** and **6** for the synthesis of  $C_3$ -symmetric AAT molecules.

### Characterisation of supramolecular assemblies

#### $C_3$ -symmetric derivatives

Given that previously prepared **1b** showed surprising self-assembly behaviour in solution and the ability to gelate organic solvents, (12) the newly synthesised AAT derivatives were tested for analogous behaviour in a representative selection of organic solvents (see Table S1 in the Supporting Information for full profile). The majority of the derivatives synthesised were exceedingly insoluble in most solvents, aside from DMF, DMSO and pyridine, a trend found for other AATs. Among the structures given in Table 1, compounds **1e**, **g** and **j** form gels (as defined by the inverted vial technique (34–36)) in a limited range of solvents upon heating (to form an isotropic phase) and cooling at ambient temperature (Figure 5). AAT **1e** form an opaque gelatinous phase in  $\text{CHCl}_3$  (Figure 5(A)) from 0.25–2 wt%, AAT **1g** forms an opaque gel in 1,1,2,2-tetrachloroethane (TCE; Figure 5(B)) from 0.25–1 wt% and AAT **1j** forms translucent gels in both toluene (Figure 5(C)) and benzene (not shown) from 0.2–3 wt%. It is worth noting that these gel phases show no evidence of dissemination over the course of several weeks.

By utilising the ‘dropping-ball’ method, (37) the  $T_{\text{gel}}$  of a 0.3 wt% solution of **1g** in TCE was measured to be 110°C – the most thermally stable gel for this class of compounds to date – while the  $T_{\text{gel}}$  of a 0.3 wt% solution of **1e** in  $\text{CHCl}_3$  was determined to be 45°C. The sol-gel transition probed in the preceding experiments was not wholly reversible; once melted, the mixture does not return to the gel state upon cooling, but must be heated to an isotropic mixture and allowed to cool again (a process that may be repeated multiple times). Unexpected given the high thermal stability exhibited by these gels, moderate shock to the formed gel resulted in an immediate

dissemination of the gel phase to a viscous suspension of the material. This behaviour contrasts with that of a 0.3 wt% (translucent) gel of **1j** in toluene ( $T_{\text{gel}} = 72^\circ\text{C}$ ). Cooling after melting of the **1j** gel results in a semi-gel

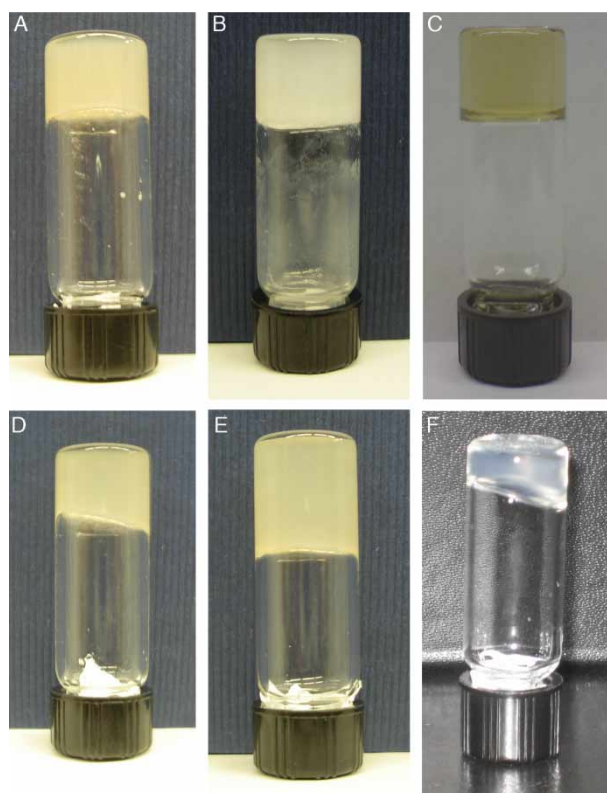


Figure 5. Inverted gels formed in sealed glass vials. (A) 0.30 wt% compound **1e** in  $\text{CHCl}_3$ , (B) 0.30 wt% compound **1g** in TCE, (C) 0.20 wt% compound **1j** in toluene, (D) 0.30 wt% of an equimolar **1e** and **1g** in TCE, (E) 0.25 wt% equimolar amounts of **1e** and **1g** in a 2:1 mixture of  $\text{CHCl}_3$ :TCE and (F) 0.40 wt% compound **1m** in  $\text{CHCl}_3$ .

(unable to support its own weight, but gelatinous), while agitation also results in a semi-gel.

Rapid access from BTF **3** to aryl amide AAT derivatives **1** with diverse aromatic substituents has encouraged the exploration of mixed AAT assemblies for the first time. This line of investigation is relatively new, but is already showing a role for complementary aromatic interactions in the self-assembly and gel-forming behaviour of the molecules. An equimolar (binary) mixture of **1e** and **1g**, e.g. forms a gel in both neat TCE (critical gelation concentration (CGC) = 0.3 wt% and  $T_{\text{gel}} = 55^\circ\text{C}$ ) and a 1:2 (w/w) TCE:CHCl<sub>3</sub> (CGC = 0.2 wt%) solution (Figures 5(D) and (E)). Of note here is that compound **1g** is unable to gel TCE below a concentration of 0.25 wt% and that compound **1e** is freely soluble in TCE up to 2 wt%, yet the combination of the two enables gelation of the solvent system. While little can be inferred with respect to molecular level ordering from this result, it does suggest that there is some complementarity between the molecules in the gel network. The ability to form mixed gels within a system unlocks the possibility for tailorability of gel morphologies and properties; this approach has already proven promising for mixed gels with H-bonding motifs (23, 38).

Samples of gels **1e** and **g** were freeze-dried (lyophilised) for imaging of the underlying morphology that could form the basis for gel networks. As is evident in the TEM micrographs (Figures 6(A)–(D)), all samples show the presence of high aspect ratio fibres common to many organogelators (36, 39–41). Fibres here can be in the order of millimetres in length, and consist of bundles (4–10) of sheets with the individual sheets averaging 200 nm in width. The fibres in the micrographs appear brittle, with fracturing and splintering of the structures at the extremes. The overall morphology contrasts with previously studied **1b** that mostly showed lamellar architectures on the nanoscale (12).

To gain better insight into the morphology of the toluene gel of **1j**, scanning electron microscopy (SEM) was used to image critical point dried (CPD) gel samples (42). In the CPD gel sample of **1j**, a lamellar sheet architecture was observed with layers of uniform thickness of about 5 μm (Figures 6(E) and (F)). The surface of the sheets reveals ~3 μm entangled fibres, and smaller fibres are observed among the entangled fibres that comprise the self-assembled network. Both fibrous and lamellar architectures have been observed earlier in the AAT systems, but this is the first case where both morphologies are visible in one sample.

While TEM and SEM techniques provide insightful nanoscale images, not necessarily observed are the architectures that best reflect the assemblies that constitute the native organogel phase (i.e. often observed are assemblies formed upon solvent evaporation that survive the freeze drying or CPD process). Structures within the

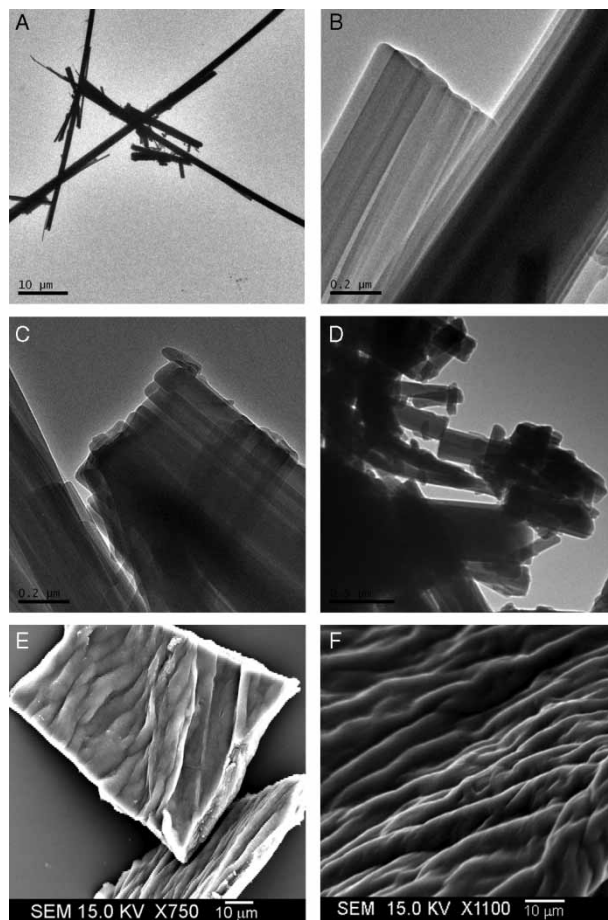


Figure 6. Micrographs of dried gels. TEM images of (A) high aspect ratio fibres formed in the freeze-dried gel of **1e**, nanoscale features within the fibres formed in the freeze-dried gel of **1e** (B) and **1g** (C); (D) fibrous aggregates formed within the mixed gel of **1e** and **1g**. (E) and (F): SEM images of the entangled fibre networks formed in the CPD gel sample of **1j**.

native gels can be imaged, albeit with lower resolution, by polarised optical microscopy (POM). The gels of **1e** in CHCl<sub>3</sub> and **1g** in TCE have been studied in this way to reveal features that are not present in the TEM micrographs (Figure 7). While the former shows a fairly uniform distribution of crystalline (birefringent) fibres, the latter shows a dual morphology. Evident in the micrograph of **1g** is spherulitic crystal growth, usually detrimental to 1-D fibrous gel formation (43); however, closer inspection also shows the presence of extremely high aspect ratio fibres dispersed throughout the sample. The longer fibres are only weakly birefringent at their edges. Quick cooling of a solution of **1g** in TCE leads to the formation of mostly well-dispersed *crystalline* fibres (not shown), and *no gel formation*. It is hypothesised that the dual morphology of the gel formed from **1g** at room temperature imparts the impressive thermal stability to this system (*vide supra*).

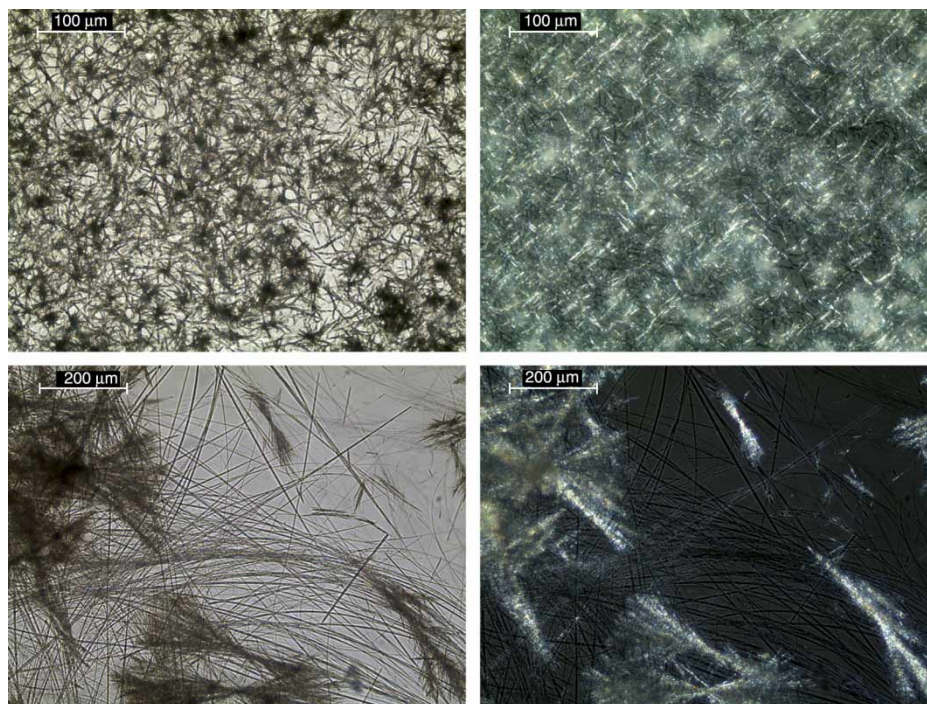


Figure 7. POM images of the native gel phases (top row is **1e** in  $\text{CHCl}_3$ ; bottom row is **1g** in TCE; the images on the right side have been taken with the polarisers crossed). Notice the distinctly different morphologies found in the two systems.

### *C<sub>s</sub>*-symmetric derivatives

*C<sub>s</sub>*-symmetric **1n** shows no evidence of gelation of the solvents tested, a result consistent with its poor solubility and lack of gelation of its AAT congeners **1a** and **1i**. Hybrid **1m** does, however, gel in  $\text{CHCl}_3$  quite efficiently (Figure 5(F)). The gel's transparency and parameters (CGC  $\sim$  0.4 wt% and  $T_{\text{gel}} \sim 50^\circ\text{C}$ ) are similar to properties previously reported for *C<sub>3</sub>*-symmetric **1b** (CGC  $\sim$  0.5 wt% and  $T_{\text{gel}} \sim 57^\circ\text{C}$ ), but obviously quite unique from non-gelator **1a**. Also, akin to transparent gels **1b** and **1j**, the **1m** gel is quite resistant to shock and maintains its shape under mild agitation.

It is anticipated that access to lower symmetry and hybrid AATs will provide a unique way to identify the structural elements most responsible for the gelation properties of this molecular class, and even an approach to rationally tune macromolecular properties. Established thus far is that AAT compounds with long alkyl chains on the periphery form more optically clear and mechanically stable gels, while the simple aryl (*13*) or aryl amide AAT derivatives form highly crystalline networks that are able to immobilise solvent. Current investigation into the rheology of AAT gels should begin to draw connections between the bulk properties, observed morphologies and molecular structures of the systems.

### Conclusions

New approaches to the synthesis of fully substituted phloroglucinols (**4**) from a common BTF, **3**, precursor have provided efficient access to previously unattainable *C<sub>3</sub>*- and *C<sub>s</sub>*-symmetric AATs (**1**). The synthetic chemistry has enabled preparation of a structurally diverse 10-component library of *C<sub>3</sub>*-symmetric aryl amide AATs, and exploration of the first binary AAT-based organogel systems. Enhanced gelation has been observed for ensembles containing AAT monomers with electronically complementary aromatic substituents (**1e** and **g**). Introduction of an expanded aromatic substituent to the AAT scaffold has provided a molecule (**1j**) that effectively immobilises aromatic solvents at low concentrations ( $\sim$  0.3 wt%). Quite uniquely, BTF also enables a stepwise approach to prepare the first differentially functionalised phloroglucinol derivatives and ultimately *C<sub>s</sub>*-symmetric AAT molecules; one derivative, **1n**, forms translucent gels at  $\sim$  0.4 wt% in chloroform. This discovery bodes well for the construction of chimeric AAT molecules for structure-property elucidation and creation of hybrid functional materials.

The organogels derived from both the *C<sub>3</sub>*- and *C<sub>s</sub>*-symmetric AAT systems have been characterised both macroscopically and on the nanoscale. Electron microscopy of the gel morphologies shows high aspect ratio fibres underlying the gel network superstructures in most cases.



POM has allowed imaging of the native organogel phases, and revealed striking morphology differences between gels that also share different optical and/or phase stability properties. Overall, access to a broader array of AATs is beginning to draw previously inaccessible relationships between structure, solubility and gel appearance/stability within this class of self-assembling molecules. Among the most alluring future lines of investigation with the AATs is their exploration in the context of supramolecular electronics (44). Efforts here will surely be leveraged by the BTF methodology that can provide molecular and supramolecular AAT structures rapidly.

## Experimental

### General

Reagents and solvents were purchased from Acros, Aldrich or Fluka, and used without further purification unless otherwise specified; 2-naphthylamine was purchased from Toronto Research Chemicals Inc. THF and DMF were degassed in 20-l drums and passed through two sequential purification columns (molecular sieves) under a positive argon atmosphere using a custom Glass Contour solvent system (Glass Contour Inc., Laguna Beach, CA, USA). Thin layer chromatography (TLC) was performed on Dynamic Adsorbents, Inc. aluminium-backed TLC plates with visualisation via UV light or staining.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Mercury 300, Gemini 300 or an Inova 500 spectrometer. Chemical shifts ( $\delta$ ) are given in parts per million (ppm) relative to residual protonated solvent ( $\text{CHCl}_3$ :  $\delta_{\text{H}}$  7.27 ppm,  $\delta_{\text{C}}$  77.00 ppm; DMSO:  $\delta_{\text{H}}$  2.50 ppm,  $\delta_{\text{C}}$  39.50 ppm; pyridine:  $\delta_{\text{H}}$  7.22, 7.58, 8.74 ppm;  $\delta_{\text{C}}$  123.9, 135.9, 150.4 ppm). Abbreviations used are s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). MS spectra (HR-MS) were acquired on a Bruker APEX II 4.7 T Fourier Transform Ion Cyclotron Resonance mass spectrometer (Bruker Daltonics, Billerica, MA, USA). DSC and TGA thermograms were taken on a Thermal Analysis DSC Q1000 and TGA Q5000, respectively. POM images were recorded by a Leica DFC295 camera using a Leica DMLP microscope coupled with a Linkham LTS350 heating stage.

### Representative gel formation

AAT **1g** (5.1 mg, 0.3% by weight) and 1,1,2,2-tetrachloroethane (TCE, 1.71 g) were combined in a sealed vial. The vial was then heated with a heat gun until a homogeneous solution was formed. The vial was then allowed to gradually cool to room temperature on the bench top, during which time the gel rapidly formed (ca. 10 min).

### Representative $T_{\text{gel}}$ determination

An organogel of **1g** in TCE with a volume of ca. 2.0 ml was prepared in a vial with a diameter of 10 mm. After the gel

had aged for 12 h at 25°C, a steel ball with a diameter of 2 mm was placed on top of the gel, the vial was resealed and placed in an oil bath. The temperature was slowly increased (ca. 0.5°C/min), and monitored using a thermometer submerged in a vial containing an equal weight of neat TCE also in the oil bath, while observing the position of the steel ball. The temperature at which the ball touched the bottom of the vial was taken as the  $T_{\text{gel}}$  temperature. This experiment was carried out thrice and the  $T_{\text{gel}}$  temperatures obtained were reproducible to within  $\pm 2^\circ\text{C}$ .

### Representative gel freeze drying procedure

A vial containing the organogel of **1g** in TCE was frozen in liquid nitrogen and transferred to a freeze dry system (Labconco FreeZone 4.5 L) overnight.

### CPD of **1f** gels

Supercritical fluid drying of **1f** gels was performed in a 3000 psi rated vessel (Parr Instruments). Samples were placed into regenerated cellulose dialysis bags with a pore diameter of 12000–14000 MWCO (Fisher Scientific, Pittsburgh, PA, USA). The samples were placed inside the drying chamber and liquid  $\text{CO}_2$  was introduced. Toluene was exchanged with liquid  $\text{CO}_2$  over 5–6 solvent exchange steps. After complete solvent removal, the vessel containing liquid  $\text{CO}_2$  was heated via a water jacket and water bath to 50°C and 1500 psi. At equilibrium, the supercritical  $\text{CO}_2$  was released from the vessel at a rate no greater than 4 l/min.

### Dried gel analysis by TEM

Some of the dried gel was flaked onto a Formvar/Carbon 200 mesh copper grid (Ted Pella Inc., Redding, CA, USA). The sample was then imaged on a JEOL TEM 200CX.

### Dried gel analysis by SEM

For all SEM experiments, a JEOL JSM 6400 scanning electron microscope was used. Samples were adhered to SEM stubs using conductive copper tape, and then sputtered with Au/Pd to improve the resolution of the images. The sputtering current was 45 mA, the Ar pressure was 75 mTorr and the sputtering time was 60 s. This yielded an Au/Pd film that was  $\sim 16$  nm thick. The SEM measurements were performed at 15 kV.

### Synthesis

*Representative synthesis of phloroglucinols from BTF: synthesis of 2,2',2''-(2,4,6-trihydroxybenzene-1,3,5-triyl)tris(N-(3,4-dimethoxyphenyl)acetamide) (**4e**)*

To a 25-ml round-bottomed flask equipped with stirbar and reflux condenser were added, BTF **3** (250 mg,

1.02 mmol) and 4-aminoveratrole (1.40 g, 9.14 mmol), followed by degassed toluene (10 ml). The reaction vessel was placed in an oil bath and heated to reflux overnight under an argon atmosphere. The solution was then cooled to room temperature and the precipitates were removed by filtration and subsequently washed with toluene, ethyl acetate and hexanes. Compound **4e** (240 mg, 33%) was obtained as a light brown solid and used without further purification.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.70 (m, 24H), 6.88 (d,  $J = 8.8$  Hz, 3H), 7.09 (dd,  $J = 8.7, 2.2$  Hz, 3H), 7.32 (d,  $J = 2.2$  Hz, 3H), 9.53 (s, 3H), 10.12 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.25, 55.31, 55.66, 103.38, 104.60, 111.39, 111.94, 132.33, 144.99, 148.46, 153.64, 171.35. HR-MS (ESI): calculated for  $\text{C}_{36}\text{H}_{40}\text{N}_3\text{O}_{12}$   $[\text{M} + \text{H}]^+$  706.2607, found 706.2608.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-phenylacetamide) (4a)*

The compound was synthesised starting from BTF (150 mg, 0.610 mmol), aniline (283 mg, 3.00 mmol) and DMF (7 ml). The reaction vessel was heated to 120°C for 15 h. Upon cooling to room temperature, the reaction mixture was poured into brine and extracted with EtOAc. The combined organic layers were washed with 1 M HCl and water, and then dried over  $\text{Na}_2\text{SO}_4$ . The solvent was removed and the residue was purified by flash column chromatography (1/3 to 1/1 EtOAc/hexanes) to yield **4a** (240 mg, 97%). The spectroscopic data match those in the literature (12).  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.71 (s, 6H), 7.05 (t,  $J = 7.5$  Hz, 3H), 7.30 (t,  $J = 7.8$  Hz, 6H), 7.61 (d,  $J = 7.8$  Hz, 6H), 9.32 (s, 3H), 10.21 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.4, 103.4, 119.3, 123.4, 128.7, 138.9, 153.6, 171.6.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(4-dodecylphenyl)acetamide) (4b)*

BTF (52 mg, 0.21 mmol) was added to a stirred solution of 4-dodecylaniline (405 mg, 1.55 mmol) in THF (5 ml). The reaction vessel was heated to reflux for 16 h. Precipitates were removed by filtration and washed with hexanes to yield **4b** (122 mg, 56%) as a white solid. The spectroscopic data match those in the literature (12).  $^1\text{H}$  NMR ( $d_6$ -DMSO/ $\text{CDCl}_3$ ):  $\delta$  0.83 (t,  $J = 6.5$  Hz, 9H), 1.21 (m, 66H), 3.70 (s, 3H), 7.04 (d,  $J = 8.5$  Hz, 6H), 7.46 (d,  $J = 8.5$  Hz, 6H), 9.71 (s, 3H), 10.11 (s, 3H).

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(4-methoxyphenyl)acetamide) (4c)*

BTF (78 mg, 0.32 mmol) and *p*-anisidine (40 mg, 3.2 mmol) were heated to reflux overnight in toluene (5 ml). Isolation of solids from the reaction mixture by

filtration and subsequent washing yielded **4c** (152 mg, 78% yield) as a white powder.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.70 (m, 15H), 6.87 (d,  $J = 8.9$  Hz, 6H), 7.50 (d,  $J = 8.9$  Hz, 6H), 9.64 (s, 3H), 10.14 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO): 32.20, 55.13, 103.41, 113.82, 121.09, 131.83, 153.69, 155.42, 171.42. HR-MS (ESI): calculated for  $\text{C}_{33}\text{H}_{34}\text{N}_3\text{O}_9$   $[\text{M} + \text{H}]^+$  616.2290, found 616.2283.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(3,5-dimethoxyphenyl)acetamide) (4d)*

BTF (150 mg, 0.62 mmol) and 3,5-dimethoxyaniline (1.16 g, 7.57 mmol) were heated to reflux overnight in THF (4 ml). After cooling to room temperature, the precipitates were removed by filtration and subsequently washed with EtOAc and hexanes. Further isolation of product from the filtrate was possible by column chromatography with a 5% MeOH:DCM eluent. The products from both purification methods were combined to yield **4d** (177 mg, 42% yield) as a light brown solid.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.69 (m, 24H), 6.20 (s, 3H), 6.86 (d,  $J = 1.9$  Hz, 6H), 9.13 (s, 3H), 10.10 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.41, 55.03, 95.44, 97.51, 103.31, 140.64, 153.55, 160.42, 171.47. HR-MS (ESI): calculated for  $\text{C}_{36}\text{H}_{40}\text{N}_3\text{O}_{12}$   $[\text{M} + \text{H}]^+$  669.2555, found 669.2594.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)acetamide) (4f)*

BTF (100 mg, 0.41 mmol) and 2,3-dihydrobenzo[b][1,4]-dioxin-6-amine (490 mg, 3.2 mmol) were combined in THF (10 mL) and the reaction vessel was heated to reflux overnight. After cooling to room temperature, the solvent was removed *in vacuo*, and the residue was redissolved in EtOAc and washed with 0.1 N HCl, deionised (DI)  $\text{H}_2\text{O}$  and then dried over  $\text{Na}_2\text{SO}_4$ . The remaining solvent was removed *in vacuo* to yield **4f** (260 mg, 91%) as a brown solid.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.66 (s, 6H), 4.20 (s, 12H), 6.77 (d,  $J = 8.6$  Hz, 3H), 6.98 (dd,  $J = 8.8$  Hz, 2.2 Hz, 3H), 7.22 (d,  $J = 2.2$  Hz, 3H), 9.49 (s, 3H), 10.07 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.23, 63.89, 64.14, 103.38, 108.59, 112.69, 116.73, 132.44, 139.48, 142.86, 153.62, 171.32. HR-MS (ESI): calculated for  $\text{C}_{36}\text{H}_{33}\text{N}_3\text{O}_{12}\text{Na}$   $[\text{M} + \text{Na}]^+$  722.1956, found 722.1947.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(4-fluorophenyl)acetamide) (4g)*

BTF (100 mg, 0.41 mmol) and *p*-fluoroaniline (400 mg, 3.66 mmol) were heated to reflux in toluene (10 ml) overnight. The solids were removed by filtration and washed with toluene, EtOAc and hexanes to yield compound **4g** (180 mg, 76%) as an off-white powder.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.69 (s, 6H), 7.14 (t,  $J = 8.8$  Hz, 6H),

7.62 (dd,  $J = 8.9, 5.0$  Hz, 6H), 9.25 (s, 3H), 10.24 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.23, 103.40, 115.26 (d,  $J = 22.6$  Hz), 121.11 (d,  $J = 7.5$  Hz), 135.32 (d,  $J = 1.3$  Hz), 153.63, 158.04 (d,  $J = 239$  Hz), 171.41. HR-MS (ESI): calculated for  $\text{C}_{30}\text{H}_{28}\text{F}_3\text{N}_4\text{O}_6$  [ $\text{M} + \text{NH}_4$ ] $^+$  602.1509, found 602.1528.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(4-methylesterphenyl)acetamide) (4h)*

BTF (200 mg, 0.81 mmol) and methyl-4-aminobenzoate (1.80 g, 12.2 mmol) were heated to reflux in THF (10 ml) over 2 days. The THF was then removed *in vacuo*, and the solids were suspended and sonicated in ethyl acetate, and isolated by filtration to yield compound **4h** (380 mg, 68%) as a white powder.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.72 (s, 6H), 3.81 (s, 9H), 7.74 (d,  $J = 8.8$  Hz, 6H), 7.91 (d,  $J = 8.8$  Hz, 6H), 8.85 (s, 3H), 10.42 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.48, 51.86, 103.29, 118.47, 123.79, 130.26, 143.60, 153.57, 165.80, 171.58. HR-MS (ESI): calculated for  $\text{C}_{36}\text{H}_{34}\text{N}_3\text{O}_{12}$  [ $\text{M} + \text{H}$ ] $^+$  700.2137, found 700.2147.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(naphthalen-2-yl)acetamide) (4i)*

BTF (86 mg, 0.35 mmol) was dissolved in DMF (5 ml) and heated to 60°C while sparging the solution with argon. 2-Naphthylamine (450 mg, 3.2 mmol) was added in one aliquot and the reaction was allowed to stir under argon at 120°C over 2 nights. The reaction mixture was cooled, poured into EtOAc and washed with 0.1 N HCl,  $\text{H}_2\text{O}$  and brine. The organic layers were dried over  $\text{Na}_2\text{SO}_4$  and the solvent was removed *in vacuo*. The residue was triturated with DCM and the insoluble material was removed by filtration and washed to yield **4i** (130 mg, 55%) as a light tan solid.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.81 (s, 6H), 7.40 (m, 3H), 7.45 (m, 3H), 7.64 (d,  $J = 8.6$  Hz, 3H), 7.79 (d,  $J = 8.1$  Hz, 3H), 7.83 (d,  $J = 8.1$  Hz, 3H), 7.86 (d,  $J = 8.8$  Hz, 3H), 8.30 (s, 3H), 9.31 (s, 3H), 10.37 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.45, 103.51, 115.52, 120.05, 124.63, 126.38, 127.30, 127.47, 128.33, 129.78, 133.36, 136.51, 153.68, 171.75. HR-MS (ESI): calculated for  $\text{C}_{42}\text{H}_{33}\text{N}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  698.2262, found 698.2253.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(7-dodecyl-naphthalen-2-yl)acetamide) (4j)*

BTF (26 mg, 0.11 mmol) and 7-dodecyl-2-aminonaphthalene (290 mg, 0.94 mmol, see Supporting Information for synthesis) were combined in THF (5 ml) and allowed to stir at reflux overnight. Upon cooling, precipitates formed in the reaction mixture were removed by filtration and washed to yield **4j** (30 mg, 25%) as a white powder.  $^1\text{H}$  NMR ( $d_5$ -pyridine):  $\delta$  0.88 (t,  $J = 6.6$  Hz, 9H), 1.32 (m,

54H), 1.68 (m, 6H), 2.73 (t,  $J = 7.2$  Hz, 6H), 4.38 (s, 6H), 7.39 (d,  $J = 8.7$  Hz, 3H), 7.89 (m, 15 H), 8.63 (s, 3H), 11.74 (s, 3H).  $^{13}\text{C}$  NMR ( $d_5$ -pyridine):  $\delta$  14.61, 23.26, 29.93, 30.14, 30.22, 30.27, 32.00, 32.44, 36.52, 105.30, 118.31, 121.61, 123.12, 126.89, 128.33, 128.72, 128.77, 131.77, 133.15, 136.82, 140.25, 155.92, 174.34. HR-MS (ESI): calculated for  $\text{C}_{78}\text{H}_{105}\text{N}_3\text{O}_6\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  1202.7901, found 1202.7805.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(3-cyanophenyl)acetamide) (4k)*

BTF (200 mg, 0.81 mmol) and 3-aminobenzonitrile (2.10 g, 17.6 mmol) were heated to reflux in dry, degassed THF over 3 nights. The reaction precipitates were removed by filtration and washed with hot EtOAc and hot *i*-PrOH to yield **4k** (175 mg, 36%) as an off-white powder.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.71 (s, 6H), 7.52 (m, 6H), 7.84 (dt,  $J = 7.0, 2.1$  Hz, 3H), 8.08 (s, 3H), 8.83 (s, 3H), 10.40 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.34, 103.29, 111.53, 118.70, 121.72, 123.64, 126.66, 130.22, 139.97, 153.58, 171.57. HR-MS (ESI): calculated for  $\text{C}_{33}\text{H}_{25}\text{N}_6\text{O}_6$  [ $\text{M} + \text{H}$ ] $^+$  601.1830, found 601.1825.

*2,2',2''-(2,4,6-Trihydroxybenzene-1,3,5-triyl)tris(N-(3-nitrophenyl)acetamide) (4l)*

BTF (75 mg, 300  $\mu\text{mol}$ ) and 3-nitroaniline (630 mg, 4.6 mmol) were heated to reflux in dry, degassed THF overnight. Precipitates from the reaction mixture were removed by filtration and washed to yield compound **4l** (80 mg, 40%) as a white powder.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  3.74 (s, 6H), 7.60 (m, 3H), 7.92 (m, 6H), 8.65 (s, 3H), 8.80 (s, 3H), 10.54 (s, 3H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  32.38, 103.30, 113.17, 117.58, 125.03, 130.13, 140.35, 147.93, 153.60, 171.60. HR-MS (ESI): calculated for  $\text{C}_{30}\text{H}_{24}\text{N}_6\text{O}_{12}\text{Na}$  [ $\text{M} + \text{Na}$ ] $^+$  683.1344, found 683.1344.

*2,2'-(2,4,6-Trihydroxy-5-(2-oxo-2-(phenylamino)ethyl)-1,3-phenylene)bis(N-(4-dodecylphenyl)acetamide) (4m)*

To a solution of compound **6** (40 mg, 120  $\mu\text{mol}$ ) in THF (5 ml) was added, 4-dodecylaniline (120 mg, 470  $\mu\text{mol}$ ). The reaction mixture was heated to 70°C overnight, after which the THF was removed *in vacuo* to yield tan solids. The crude material was dissolved in hot EtOAc/hexanes and allowed to slowly precipitate upon cooling. Filtration and washing with 0.1 N HCl yielded **4m** (61 mg, 59%) as a waxy, off-white solid.  $^1\text{H}$  NMR ( $d_6$ -DMSO):  $\delta$  0.84 (t,  $J = 6.4$  Hz, 6H), 1.23 (br s, 36H), 1.52 (m, 4H), 3.70 (br s, 6H), 7.06 (m, 5H), 7.29 (t,  $J = 7.9$  Hz, 2H), 7.48 (d,  $J = 8.5$  Hz, 4H), 7.60 (d,  $J = 7.9$  Hz, 2H), 9.43 (m, 3H), 10.12 (s, 2H), 10.17 (s, 1H).  $^{13}\text{C}$  NMR ( $d_6$ -DMSO):  $\delta$  13.94, 22.07, 28.55, 28.68, 28.83, 28.97, 29.00, 30.95,

31.27, 32.31, 34.52, 103.41, 103.49, 119.37, 119.49, 123.38, 128.39, 128.68, 136.43, 137.48, 138.90, 153.65, 171.52. HR-MS (ESI): calculated for  $C_{54}H_{76}N_3O_6$   $[M + H]^+$  862.5729, found 862.5719.

*2,2'-(2,4,6-Trihydroxy-5-(2-(naphthalen-2-ylamino)-2-oxoethyl)-1,3-phenylene)bis(N-phenylacetamide) (4n)*

A stirring solution of **5** (86 mg, 0.20 mmol) in DMF (5 ml) was treated with 2-naphthylamine (34 mg, 0.24 mmol) and heated to 120°C for 12 h. The solvent was removed *in vacuo* and the residue was dissolved in ethyl acetate. The organic layer was washed with 10% HCl and water. The combined organic layers were dried with  $Na_2SO_4$ . The solvent was then removed *in vacuo* and the crude product was purified via column chromatography (hexane/EtOAc 1:1) to afford **4n** (80 mg, 70%) as a yellow solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  3.73 (s, 4H), 3.78 (s, 2H), 7.05 (t,  $J = 7.5$  Hz, 2H), 7.30 (t,  $J = 7.5$  Hz, 4H), 7.43 (m, 2H), 7.62 (m, 5H), 7.85 (m, 3H), 8.28 (s, 1H), 9.31 (s, 2H), 9.32 (s, 1H), 10.19 (s, 2H), 10.37 (s, 1H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  13.58, 20.26, 31.86, 59.25, 102.94, 105.26, 115.01, 117.88, 118.85, 119.55, 120.32, 122.91, 124.5, 125.33, 125.8, 125.9, 126.82, 126.95, 127.84, 127.96, 128.23, 129.29, 132.87, 134.49, 136.02, 138.41, 146.14, 153.15, 171.09, 171.26. HR-MS (ESI): calculated for  $C_{34}H_{29}N_3O_6Na$   $[M + Na]^+$  598.1949, found 598.1944.

*Representative procedure for the synthesis of AATs from phloroglucinols: synthesis of N-(3,4-dimethoxyphenyl)-2-(4,6,10-trioxo-5,7-di-3,4-dimethoxyphenylcarbamoylmethyl-1-aza-tricyclo[3.3.1.1.3,7]dec-3-yl)-acetamide (1e)*

To a 10-ml round-bottomed flask with stirbar and reflux condenser was added, compound **4e** (125 mg, 0.180 mmol) followed by HMTA (75 mg, 0.53 mmol) and degassed *i*-PrOH (4 ml). The reaction vessel was then placed in an oil bath and allowed to reflux with stirring overnight under an argon atmosphere. The next day, the reaction vessel was allowed to cool to room temperature and the precipitates were removed by filtration and washed with *i*-PrOH (1 ml). The solids were then resuspended in ethyl acetate (10 ml), sonicated and filtered to yield compound **1e** (75 mg, 53%) as a slightly tan solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.73 (br s, 6H), 3.69 (br s, 18H), 3.93 (br s, 6H), 6.84 (d,  $J = 8.8$  Hz, 3H), 7.01 (dd,  $J = 8.6, 1.6$  Hz, 3H), 7.27 (d,  $J = 1.6$  Hz, 3H), 9.87 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO): 33.66, 55.35, 55.73, 70.21, 70.37, 104.08, 110.74, 112.06, 133.07, 144.54, 148.49, 167.15, 198.27. HR-MS (ESI): calculated for  $C_{39}H_{43}N_4O_{12}$   $[M + H]^+$  759.2872, found 759.2902.

*2,2',2''-((3s,5s,7s)-4,6,10-Trioxo-1-azaadamantane-3,5,7-triyl)tris(N-(4-methoxyphenyl)acetamide) (1c)*

To a solution of **4c** (99 mg, 0.16 mmol) in *i*-PrOH (5 ml) was added, HMTA (60 mg, 0.43 mmol) and the solution

was brought to reflux over 3 nights under argon. Precipitates formed during the reaction were removed by filtration and washed, yielding **1c** (37 mg, 34%) as a white solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.68 (s, 6H), 3.65 (s, 9H), 3.86 (s, 6H), 6.78 (d,  $J = 8.7$  Hz, 6H), 7.39 (d,  $J = 8.7$  Hz, 6H), 9.81 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  33.55, 55.10, 70.18, 70.31, 113.69, 120.36, 132.54, 154.88, 167.04, 198.32. HR-MS (ESI): calculated for  $C_{36}H_{37}N_4O_9$   $[M + H]^+$  669.2555, found 669.2594.

*2,2',2''-((3s,5s,7s)-4,6,10-Trioxo-1-azaadamantane-3,5,7-triyl)tris(N-(3,5-dimethoxyphenyl)acetamide) (1d)*

To *i*-PrOH (5 ml) was added, **4d** (99 mg, 0.14 mmol), followed by HMTA (56 mg, 0.40 mmol), and the reaction mixture was heated to reflux for 2 days. After cooling to room temperature, isolation and washing of the precipitates from the reaction mixture yielded **1d** (11 mg, 11%) as a light orange solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.74 (s, 6H), 3.68 (s, 18H), 3.92 (s, 6H), 6.16 (s, 3H), 6.79 (d,  $J = 1$  Hz, 6H), 9.98 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  25.48, 33.79, 55.03, 70.16, 95.09, 97.10, 140.96, 160.41, 167.63, 198.13. HR-MS (ESI): calculated for  $C_{36}H_{40}N_3O_{12}$   $[M + H]^+$  759.2872, found 759.2877.

*2,2',2''-((3s,5s,7s)-4,6,10-Trioxo-1-azaadamantane-3,5,7-triyl)tris(N-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)acetamide) (1f)*

To a solution of **4f** (100 mg, 0.15 mmol) in *i*-PrOH (5 ml) was added, HMTA (64 mg, 0.46 mmol) and the reaction vessel was heated to reflux overnight. Precipitates from the reaction mixture were removed by filtration, resuspended in EtOAc and filtered again with washing to yield **1f** (44 mg, 40%) as a light brown solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.70 (s, 6H), 3.89 (s, 6H), 4.19 (d,  $J = 6.5$  Hz, 12H), 6.73 (d,  $J = 8.6$  Hz, 3H), 6.92 (dd,  $J = 8.1$  Hz, 2.2 Hz, 3H), 7.15 (d,  $J = 2.2$  Hz, 3H), 9.82 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  33.61, 63.88, 64.16, 70.32, 70.15, 107.96, 112.10, 116.60, 133.05, 138.95, 142.84, 167.07, 198.25. HR-MS (ESI): calculated for  $C_{39}H_{37}N_4O_{12}$   $[M + H]^+$  753.2403, found 753.2398.

*N-(4-Fluorophenyl)-2-(4,6,10-trioxo-5,7-di-4-fluorophenyl-carbamoylmethyl-1-aza-tricyclo[3.3.1.1.3,7]dec-3-yl)-acetamide (1g)*

To a solution of **4g** (95 mg, 160  $\mu$ mol) in *i*-PrOH was added, HMTA (69 mg, 490  $\mu$ mol) and the mixture was heated to reflux overnight. Removal of the solids by filtration and subsequent washing yielded **1g** (33 mg, 35%) as a white powder.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.76 (s, 6H), 3.92 (s, 6H), 7.10 (t,  $J = 8.8$  Hz, 6H), 7.54 (dd,  $J = 8.7, 5.0$  Hz, 6H), 10.07 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  25.48,

33.61, 70.17, 115.12 (d,  $J = 22.3$  Hz), 120.52 (d,  $J = 7.7$  Hz), 135.73, 157.71 (d,  $J = 238$  Hz), 167.45, 198.25. HR-MS (DART): calculated for  $C_{33}H_{28}F_3N_4O_6$   $[M + H]^+$  633.1961, found 633.1979.

*N*-(4-Methylesterphenyl)-2-(4,6,10-trioxo-5,7-di-4-methyl-esterphenylcarbamoylmethyl-1-aza-tricyclo[3.3.1.1.3,7]dec-3-yl)-acetamide (**1h**)

To a solution of **4h** (42 mg, 60  $\mu$ mol) in *i*-PrOH was added, HMTA (25 mg, 180  $\mu$ mol) and the reaction mixture was heated to reflux over 3 nights. Solids from the reaction mixture were removed by filtration, then washed and dried to yield compound **1h** (10 mg, 21%) as a slightly tan powder.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.82 (s, 6H), 3.81 (s, 9H), 3.93 (s, 6H), 7.67 (d,  $J = 7.7$  Hz, 6H), 7.88 (d,  $J = 7.4$  Hz, 6H), 10.40 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  33.81, 51.73, 70.16, 70.37, 118.17, 123.55, 130.15, 143.57, 165.74, 168.05, 198.27. HR-MS (ESI): calculated for  $C_{39}H_{37}N_4O_{12}$   $[M + H]^+$  753.2402, found 753.2416.

2,2',2''-((3s,5s,7s)-4,6,10-Trioxo-1-azaadamantane-3,5,7-triyl)tris(*N*-(naphthalen-2-yl)acetamide) (**1i**)

To a solution of **4i** (49 mg, 0.072 mmol) in *i*-PrOH was added, HMTA (30 mg, 0.22 mmol) and the reaction mixture was heated to reflux for 120 h. After cooling, the insoluble material was isolated, triturated with EtOAc, isolated by filtration and washed to yield **1i** (35 mg, 66%) as a slightly tan solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.88 (s, 6H), 4.00 (s, 6H), 7.37 (m, 3H), 7.44 (t,  $J = 7.5$  Hz, 3H), 7.52 (d,  $J = 8.6$  Hz, 3H), 7.80 (m, 9H), 8.29 (s, 3H), 10.24 (s, 3H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  33.84, 70.28, 70.46, 114.74, 119.80, 124.35, 126.31, 127.19, 127.38, 128.22, 129.54, 133.44, 136.51, 167.61, 198.31. HR-MS (ESI): calculated for  $C_{45}H_{36}N_4O_6Na$   $[M + Na]^+$  751.2517, found 751.2517.

2,2',2''-((3s,5s,7s)-4,6,10-Trioxo-1-azaadamantane-3,5,7-triyl)tris(*N*-(7-dodecyl-naphthalen-2-yl)acetamide) (**1j**)

To a solution of **4j** (25 mg, 0.021 mmol) in *i*-PrOH was added, HMTA (8.8 mg, 0.063 mmol) and the reaction mixture was allowed to reflux for 120 h. After cooling, the insoluble material was isolated, triturated with EtOAc, again isolated by filtration and washed to yield **1j** (17 mg, 65%) as a white powder.  $^1H$  NMR ( $d_5$ -pyridine):  $\delta$  0.87 (t,  $J = 6.9$  Hz, 9H), 1.29 (m, 60H), 1.67 (m, 6H), 2.73 (t,  $J = 7.6$  Hz, 6H), 4.37 (s, 6H), 7.38 (d,  $J = 8.2$  Hz, 3H), 7.68 (s, 3H), 7.8 (d,  $J = 8.5$  Hz, 3H), 7.87 (m, 6H), 8.61 (s, 3H), 11.73 (s, 3H).  $^{13}C$  NMR ( $d_5$ -pyridine):  $\delta$  14.98, 23.63, 26.75, 28.34, 30.30, 30.33, 30.53, 30.60, 30.65, 32.40, 32.81, 36.90, 72.11, 75.87, 117.39, 121.57, 127.24, 128.55, 129.02, 131.75, 133.74, 140.11, 169.59, 200.21. HR-MS (ESI): calculated for  $C_{81}H_{108}N_4O_6Na$   $[M + Na]^+$  1255.8167, found 1255.8136.

2,2'-((1s,3r,5s,7r)-4,6,10-Trioxo-7-(2-oxo-2-(phenylamino)ethyl)-1-azaadamantane-3,5-diyl)bis(*N*-(4-dodecylphenyl)acetamide) (**1m**)

To a solution of **4m** (51 mg, 59  $\mu$ mol) in *i*-PrOH was added, HMTA (17 mg, 120  $\mu$ mol) and the reaction mixture was allowed to reflux over 2 nights. After cooling, the insoluble material was isolated by filtration and washed with 0.1 N HCl, *i*-PrOH and EtOAc before being dried *in vacuo* to yield **1m** (30 mg, 56%) as a white, flaky solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  0.85 (t,  $J = 6.7$  Hz, 6H), 1.23 (br s, 36H), 1.52 (m, 4H), 2.77 (m, 6H), 3.91 (m, 6H), 7.00 (t,  $J = 7.3$  Hz, 1H), 7.05 (d,  $J = 8.2$  Hz, 4H), 7.25 (t,  $J = 7.8$  Hz, 2H), 7.41 (d,  $J = 8.1$  Hz, 4H), 7.53 (d,  $J = 8.0$  Hz, 2H), 9.82 (s, 2H), 9.93 (s, 1H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  13.76, 21.92, 28.41, 28.52, 28.69, 28.82, 28.85, 30.83, 31.12, 33.57, 34.38, 70.11, 70.23, 118.85, 118.92, 122.72, 128.10, 128.40, 136.67, 136.84, 139.18, 167.18, 167.41, 198.12, 198.16. HR-MS (ESI): calculated for  $C_{57}H_{79}N_4O_6$   $[M + H]^+$  915.5994, found 915.5981.

2,2'-((1r,3r,5s,7s)-7-(2-(Naphthalen-2-ylamino)-2-oxoethyl)-4,6,10-trioxo-1-azaadamantane-3,5-diyl)bis(*N*-phenylacetamide) (**1n**)

A solution of **4n** (90 mg, 0.16 mmol), HMTA (66 mg, 0.48 mmol) and *i*-PrOH (5 ml) was heated to reflux for 2 days. After cooling to room temperature, the mixture was filtered to afford an off-white solid. The solid was washed with 5% HCl and water to afford **1n** (41 mg, 43%) as an off-white solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  2.79 (s, 4H), 2.85 (s, 2H), 3.95 (s, 6H), 6.99 (t,  $J = 7.5$  Hz, 2H), 7.26 (t,  $J = 7.8$  Hz, 4H), 7.45 (m, 8H), 7.81 (m, 3H), 8.27 (s, 1H), 10.01 (s, 2H), 10.23 (s, 1H).  $^{13}C$  NMR ( $d_6$ -DMSO):  $\delta$  33.21, 69.71, 69.88, 114.19, 118.35, 119.28, 122.33, 123.85, 125.81, 126.69, 126.88, 127.72, 128.08, 129.03, 132.95, 136.36, 138.80, 167.03, 167.28, 197.79. HR-MS (ESI): calculated for  $C_{37}H_{32}N_4O_6Na$   $[M + Na]^+$  651.2214, found 651.2208.

2,2'-(4,6-Dihydroxy-2-oxo-2,3-dihydrobenzofuran-5,7-diyl)bis(*N*-phenylacetamide) (**5**)

To a solution of BTF (100 mg, 0.40 mmol) in DMF (2 ml) was added dropwise, aniline solution (3.2 ml of a 0.5 M solution, 1.6 mmol). The resulting solution was stirred over 2 nights in a 70°C oil bath, after which the reaction was diluted with EtOAc (200 ml), washed with 0.3 N HCl, DI H<sub>2</sub>O, then brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* and the residue was purified by column chromatography (1/10 acetone/DCM) to yield **5** (79 mg, 45%) as an off-white solid.  $^1H$  NMR ( $d_6$ -DMSO):  $\delta$  3.67 (s, 2H), 3.68 (s, 2H), 3.74 (s, 2H), 7.03 (q,  $J = 7.6$  Hz, 2H), 7.34–7.23 (m, 4H), 7.59 (d,  $J = 7.9$  Hz, 4H), 9.55 (s, 1H), 9.70 (s, 1H), 10.05 (s, 1H), 10.24 (s,

1H). <sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO): δ 31.63, 31.77, 31.92, 98.43, 100.53, 106.69, 119.02, 119.25, 123.00, 123.37, 128.65, 128.70, 138.92, 139.27, 150.45, 152.18, 155.02, 169.69, 170.31, 174.63. HR-MS (ESI): calculated for C<sub>24</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub> [M + H]<sup>+</sup> 433.1394, found 433.1389.

*2-(4-Hydroxy-2,7-dioxo-2,3,7,8-tetrahydrobenzo[1,2-b:3,4-b']difuran-5-yl)-N-phenylacetamide (6)*

To a solution of BTF (100 mg, 0.40 mmol) in DMF (600 μl) was added dropwise, aniline solution (560 mg in 12 ml DMF, 6.0 mmol). The resulting solution was allowed to stir for 8 h in a 40°C oil bath. The reaction mixture was next diluted with EtOAc (200 ml), washed with 0.3 N HCl, DI H<sub>2</sub>O, then brine and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was removed *in vacuo* and the residue was purified by column chromatography (1/20 acetone/DCM) to yield **6** (76 mg, 56%) as an off-white solid. <sup>1</sup>H NMR (*d*<sub>6</sub>-DMSO): δ 3.66 (s, 2H), 3.80 (s, 2H), 3.95 (s, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 7H), 10.07 (s, 1H), 10.13 (s, 1H). <sup>13</sup>C NMR (*d*<sub>6</sub>-DMSO): δ 30.6, 31.1, 31.4, 97.1, 102.6, 104.8, 118.9, 123.0, 128.7, 139.2, 147.8, 151.3, 153.7, 168.3, 173.9, 174.1. HR-MS (ESI): calculated for C<sub>18</sub>H<sub>15</sub>NO<sub>6</sub> [M + H]<sup>+</sup> 340.0816, found 340.0813.

### Supplementary materials

Details of the synthesis of 7-dodecyl-2-aminonaphthalene, solubility and gelation profiles for selected AAT derivatives, and copies of the <sup>1</sup>H NMR spectra for all new compounds are available online.

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