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Triflic Acid-Promoted Adamantylation and *tert*-Butylation of Pyrene: Fluorescent Properties of Pyrene-Decorated Adamantanes and a Channeled Crystal Structure of 1,3,5-Tris(pyren-2-yl)adamantane

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Cite This: *J. Org. Chem.* 2020, 85, 11134−11139 Read Online

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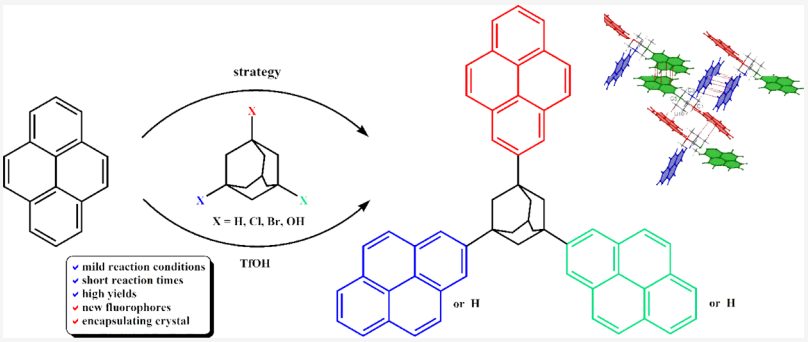


ABSTRACT: Triflic acid-promoted 1-adamantylation and *tert*-butylation of pyrene at positions **2** and **2,7** along with the synthesis of compounds having one-, two-, and three-pyrenyl groups attached to the adamantane scaffold are disclosed. Fluorescent properties of these compounds and channeled crystal structure of the 1,3,5-tris(pyren-2-yl)adamantane containing chloroform as a guest are also presented.

INTRODUCTION

Pyrene **1** (Figure 1) is a fascinating fluorophore[1] and one of the most promising starting materials for preparing a plethora

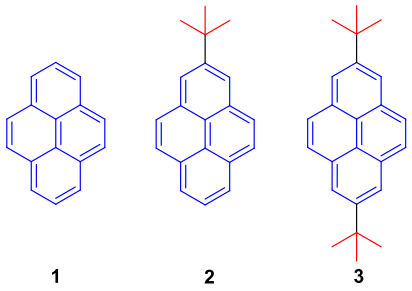


Figure 1. Formulae of compounds **1**−**3**.

of organic optoelectronic materials.[2] Two alkyl-substituted pyrene derivatives, 2-*tert*-butylpyrene **2** and 2,7-di-*tert*-butylpyrene **3**, have been widely used as useful starting materials in numerous syntheses of dyes that feature special molecular shapes and suppressed aggregation properties.[3] Moreover, the latter compound proved to be an efficient acceptor for triplet−triplet annihilation[4] and a π−donor for semiconductive charge-transfer cocrystals.[5] To date, both compounds could be obtained via Friedel−Crafts alkylation of pyrene with *tert*-butyl chloride in the presence of a Lewis acid (aluminum chloride or bromide). This reaction is unusual because electrophiles usually attack pyrene at positions 1, 3, 6, or 8.[2a] Moreover, there have been no reports on the extension of its scope to other alkyl halides.

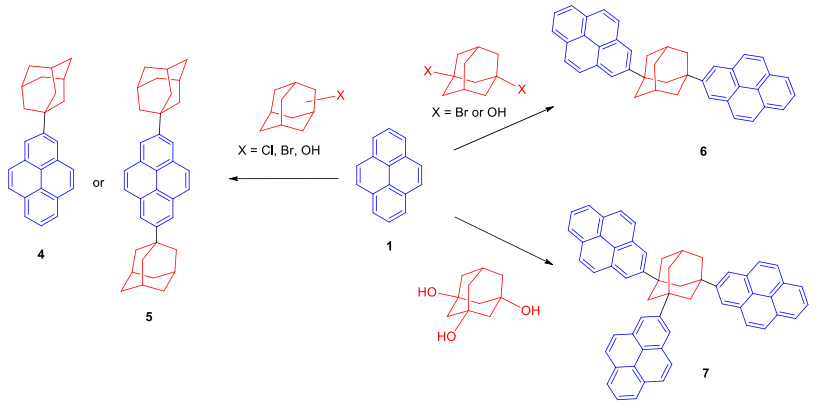
RESULTS AND DISCUSSION

In continuation of our earlier work on triflic acid (TfOH)-promoted Friedel−Crafts pyrene chemistry,[6] we became interested in elaborating a synthetic route to pyrenes bearing other bulky tertiary alkyl groups at C(2) and C(7) using this superacid as a promoter. The adamantyl group seemed especially interesting because physicochemical properties of adamantyl-substituted compounds may be different from those of their *tert*-butyl-substituted counterparts.[7] Moreover, in contrast to the *tert*-butyl group, the rigid adamantane scaffold offers a possibility of attachment, via the Friedel−Crafts chemistry, of the two, three, or four aryl group to the tertiary carbons. It has been demonstrated that di-, tri-, and tetraaryl

Received: April 30, 2020
Published: August 7, 2020

https://dx.doi.org/10.1021/acs.joc.0c01060
J. Org. Chem. 2020, 85, 11134−11139

Table 1. Optimized Conditions for the Adamantylation of Pyrene



entry	AdaX	pyrene/AdaX/TfOH (mmol)	reaction time	product (isolated yield, %)[a]
1	1-AdaBr	1:1:4	5 min	**4** (93)
2	1-AdaOH	1:1:4	5 min	**4** (84)
3	1-AdaBr	1:2.2:4	30 min	**5** (91)
4	1-AdaCl	1:2.2:4	30 min	**5** (87)
5	1-AdaOH	1:2.2:4	1 h	**5** (95)
6	2-AdaBr	1:2.2:4	30 min	**5** (83)
7	2-AdaOH	1:2.2:4	1 h	**5** (87)
8	1,3-AdaBr$_2$	3:1:12	4 h	**6** (62)
9	1,3-Ada(OH)$_2$	3:1:12	4 h	**6** (49)
10	1,3,5-Ada(OH)$_3$	4.5:1:18	6 h	**7** (63)

[a]Reactions were carried out in dichloromethane (10 mL) at r.t.; Ada = adamantyl.

adamantanes have a great tendency to form various types of supramolecular systems in the solid state (e.g., encapsulating crystals[8] and were used in syntheses of porous aromatic frameworks).[9] The adamantane skeleton was also used as a rigid linker between chromophoric groups.[10] Therefore, molecules bearing several pyrenyl groups in a well-defined spatial arrangement might be of interest for developing solid-state emitters, sensors, or self-assembled nanomaterials.

In this study, we report the results of this research along with the basic fluorescent properties of the synthesized pyrene derivatives **4**–**7** (Table 1) and the crystal structure of tripyrenyladamantane **7** encapsulating molecule of the solvent (chloroform).

We found that pyrene **1** smoothly reacts with 1-adamantanol or 1-bromoadamantane in the presence of excess of TfOH in dichloromethane at room temperature to afford, depending on the reaction conditions, compound **4** or **5**. To obtain pure **4**, not contaminated with **5**, pyrene and adamantyl compound were used at a molar ratio of 1:1 and the reaction was stopped after 5 min (entries 1 and 2). On the other hand, at the pyrene to adamantyl compound molar ratio of 1:2.2 and prolonged reaction times (30 min to 1 h), diadamantylpyrene **5** was formed in high yields (entries 3–7). It is also worthy to note that compound **4** can also be obtained in practically the same yield using 2-bromoadamantane or 2-adamantanol as alkylating agents (Table 1, entries 6 and 7). This suggests the intermediacy of the 2-adamantyl cation, which is known to rapidly isomerize to its 1-isomer.[11,12]

Having in hand an efficient protocol for the synthesis of **4** and **5**, we became interested in its application for the synthesis of compounds having two and three pyrenyl units linked to the adamantane skeleton. To our pleasure, we found that the reaction of 3 equiv of pyrene with 1,3-dibromoadamantane or adamantane-1,3-diol in the presence of TfOH yielded, after 4 h, 1,3-bis(pyren-2-yl)adamantane **6** in 62 and 49% yield, respectively (entries 8 and 9). Furthermore, the reaction of 4.5 equiv of pyrene with adamantane-1,3,5-triol gave, after 6 h, 1,3,5-tris(pyren-2-yl)adamantane (**7**) in 63% yield (Table 1, entry 10).

We also found out that our protocol can be used for alternative synthesis of *tert*-butylpyrenes **2** and **3** (see the Supporting Information for details). Both *tert*-butyl halides and *tert*-butanol afford the expected products in high yields (86–96%). In our opinion, this procedure is more convenient than the procedures described in literature, which use aluminum halides as promoter.

Formation of the 2- and 2,7-substituted products in the reaction of pyrene with *tert*-butyl halides is usually explained to be due to bulkiness of the *tert*-butyl group (these positions are relatively less sterically hindered).[2a] In our opinion, the same explanation may be valid for reactions with adamantyl compounds.

We studied electronic absorption and emission spectra of compounds **2**–**7**. The spectra obtained for diluted solutions in dichloromethane are shown in Figure 2 (the table contains the photophysical data in the Supporting Information).

All investigated compounds showed absorption and emission bands assignable to the isolated, monomeric pyrene fluorophore. There was no evidence for the formation of intramolecular excimers by **6** and **7** (negligible emission at ~450 nm). This means that the rigid adamantane skeleton efficiently keeps pyrenyl moieties electronically isolated from each other. However, there was a significant difference in the solid-state emission of compounds **3** and **5** (normalized emission spectra in the solid state in the Supporting Information). While the former compound showed the structured emission characteristic of isolated pyrene fluorophore, the latter displayed excimer emission (λ_{max} ~ 450 nm).

https://dx.doi.org/10.1021/acs.joc.0c01060
J. Org. Chem. 2020, 85, 11134–11139

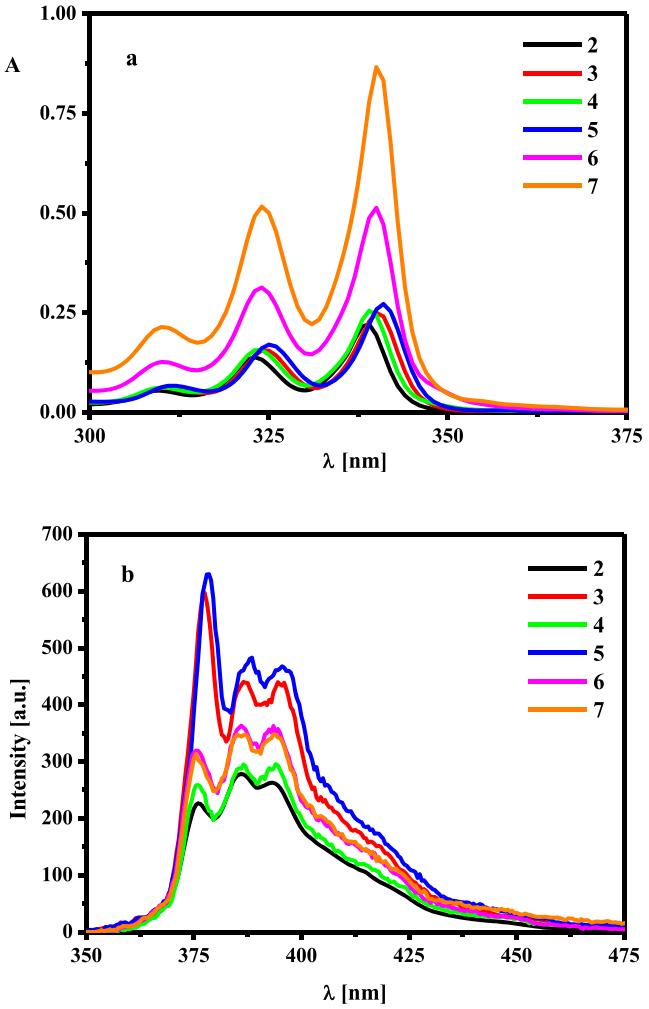


Figure 2. Electronic absorption (a) and emission (b) spectra of compounds **2**–**7** in argon-saturated dichloromethane solutions. Absorption spectra were run at $c = 5 \times 10^{-6}$ M. Emission spectra were obtained with an excitation at 340 nm for a solution having the same absorbance (0.10) at this wavelength.

Therefore, the 1-adamantyl group, unlike the *tert*-butyl group, does not protect 2,7-disubstituted pyrene against the aggregation.

Unexpectedly, we found that solution of **7** in $CDCl_3$ in an NMR tube slowly deposited crystals in the form of large, yellowish elongated blocs. They tended to lose transparency and transform into a powder within seconds after extracting from the mother solution. Nevertheless, we succeeded in X-ray diffraction structure determination of a single crystal suspended in a drop of the solvent. The molecular structure of **7** is shown in Figure 3. The three pyrene units are differently inclined with respect to the idealized plane containing the main adamantane axis and C10 and H10 atoms. The inclination angles are 67.4(5)°, 15.6(6)°, and 21.9(5)° for pyrene moieties I, II, and III, respectively. They also show some deviation from planarity and are to some extent bent roughly along the short pyrene axis. The angles between the average planes of the terminal rings within the pyrene fragments are 4.2(3)°, 2.9(3)°, and 6.9(3)° for pyrenes I, II, and III, respectively.

The crystal contains infinite channels (~7.5% of the unit cell volume) spreading in the [100] direction filled with highly disordered chloroform molecules (Figure 4).

Analysis of intermolecular interactions in the crystal of **7** shows that pyrene II and III moieties are involved in a partial $\pi-\pi$ stacking with their inversion-related counterparts (inter-ring distances are equal to 3.402(4) Å for pyrene II and 3.489(5) Å for pyrene III). On the other hand, pyrene I is involved in a C10–H10$\cdots\pi$ stacking interaction with the adamantane core of the inversion-related molecule. The distance between the planes of the symmetry-related pyrenes in that case is as long as 5.318(4) Å (Figure 5).

The transformation of the crystals of **7** into a powder is caused by the loss of the chloroform guest, which apparently stabilizes the crystal structure. Therefore, this compound is able to bind chloroform in its crystal structure in chloroform solution and release it when chloroform is absent in the surrounding medium. Such a behavior promises possible applications of **7** and its derivatives as crystal containers for various substances. In addition, it is worthy to note that all of the synthesized pyrenyladamantanes are expected to be easily functionalized by electrophilic substitution, making possible a tuning of their photophysical and supramolecular properties.

In conclusion, we have elaborated a simple and efficient synthetic route for introduction of *tert*-butyl and 1-adamantyl groups into positions 2- and 2,7- of pyrene. It allowed synthesis of compounds having two- and three-pyrenyl groups attached to the adamantane scaffold. They show a solvent-dependent pyrene-like fluorescence, which may be of interest for various applications. Furthermore, a synthesized tripyrenyladamantane is able to reversibly bind and release chloroform in the solid state. Future work will consist of derivatization of the synthesized pyrenyladamantanes and testing their ability to bind various guests in the solid state.

EXPERIMENTAL SECTION

General Remarks. Solvents were purified prior to use by reported methods. All reagents were purchased from Sigma-Aldrich and used without further purification. The reaction progress was monitored by means of thin-layer chromatography, which was performed on aluminum foil plates covered with silica gel 60 F_{254}. Column chromatography was performed on silica gel 60 (0.040–0.063 mm, 230–400 mesh, Fluka). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker ARX 600 MHz (600 MHz for ^{1}H and 151 MHz for ^{13}C). Chemical shifts were referenced relative to solvent signals: δ = 7.26 ppm for ^{1}H and δ = 77.00 ppm for ^{13}C. Spectra were recorded at room temperature (291 K), chemical shifts are presented in parts per million, and coupling constants are presented in hertz. Electronic absorption spectra were run on a PerkinElmer Lambda 45 UV/vis spectrometer. Corrected emission spectra were obtained on a PerkinElmer LS55 fluorescence spectrometer. The emission quantum yields were determined for argon-purged solutions using quinine sulfate in 0.5 M sulfuric acid (Φ_F = 0.546) as a reference.

General Procedure for the Synthesis of 2–7. Alkylating agent RX (for amounts of reactants, see Tables S1 or S2) and TfOH were added to a solution of pyrene in 10 mL of CH_2Cl_2 at room temperature. After stirring for 5 min to 6 h (Tables S1, S2), the reaction mixture was poured into water (100 mL) and extracted several times with dichloromethane. The combined extracts were dried over anhydrous Na_2SO_4 and evaporated to dryness. The crude products were purified by column chromatography on silica gel (hexane or petroleum ether/ethyl acetate as eluent) to give the desired products.

*2-tert-Butylpyrene (**2**).* Purification by chromatography eluting with petroleum ether/ethyl acetate (95/5, v/v) gave **2** [248 mg, 96% (Table S2, entry 2)] as a white powder. mp 110–111 °C (lit.[13] mp 110–112 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.27 (s, 2H), 8.18 (d, J = 7.8 Hz, 2H), 8.10 (d, J = 8.7 Hz, 2H), 8.08 (d, J = 8.7 Hz, 2H), 8.00 (t, J = 7.8 Hz, 1H), 1.64 (s, 9H); ^{13}C{^{1}H} NMR (151 MHz,

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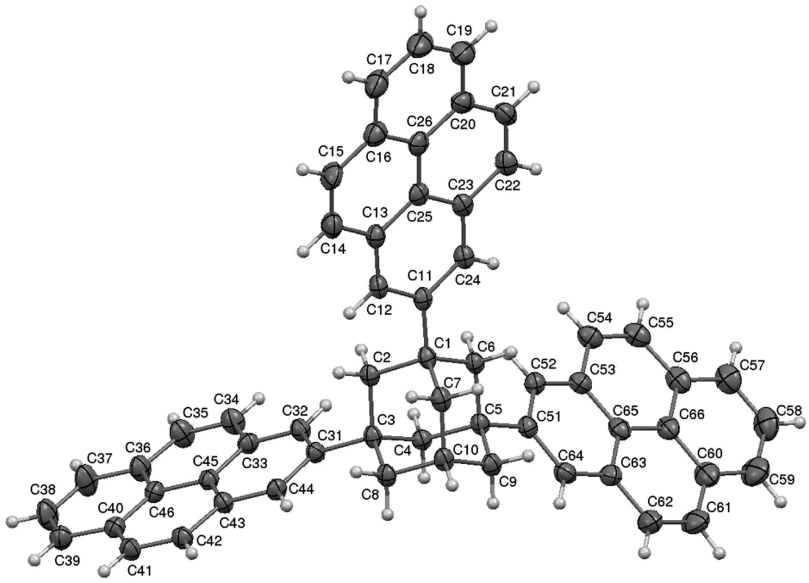

Figure 3. Molecular structure of 7. Atomic displacement parameters represented at the 50% probability level. C atoms numbered 11−26 constitute pyrene I, C atoms 31−46 constitute pyrene II, and C atoms 51−66 constitute pyrene III moieties.

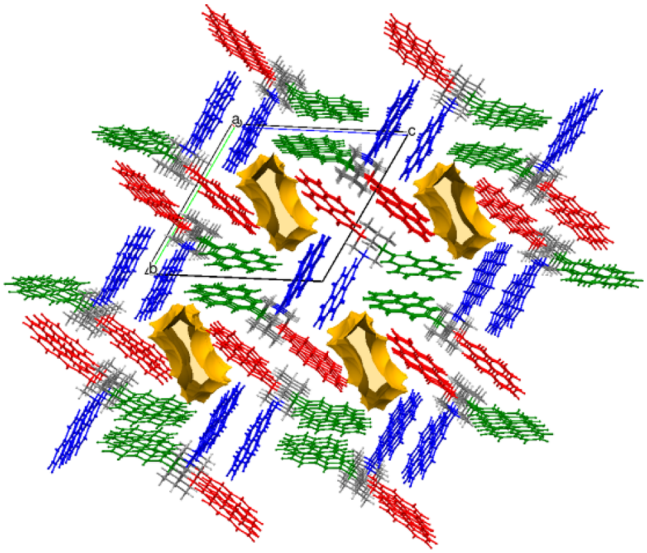

Figure 4. Crystal packing of 7 viewed in the [100] direction. Pyrenes I, II, and III are highlighted in red, blue, and green. The disordered molecules of chloroform occupy channels highlighted in yellow.

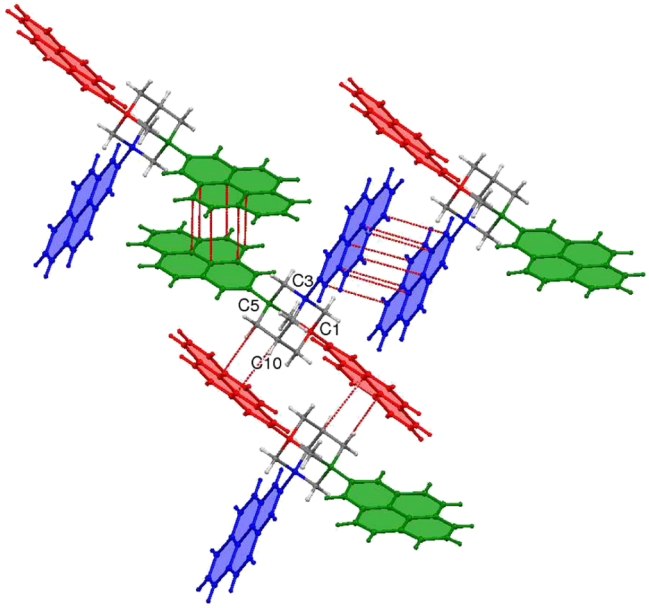

Figure 5. Most important intermolecular interactions formed by 7 in the crystal structure viewed along [100]. Interatomic distances shorter than the sum of the van der Waals radii are presented as red dashed lines.

$CDCl_3$): δ 148.9, 130.9, 130.9, 127.5, 127.2, 125.5, 124.7, 124.6, 122.9, 122.1, 35.2, 31.9. MS (EI) m/z: 259 $[M]^+$, 281 $[M + Na]^+$; anal. Calcd for $C_{20}H_{18}$: C, 92.98; H, 7.02. Found: C, 92.77; H, 6.91.

*2,7-Ditert-butylpyrene (**3**).* Purification by chromatography eluting with petroleum ether/ethyl acetate (95/5, v/v) gave **3** [289 mg, 92% (Table S2, entry 5)] as a white powder. mp 210−212 °C (lit.[14] mp 210−212 °C). ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.19 (s, 4H), 8.03 (s, 4H), 1.59 (s, 18H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 148.5, 130.8, 127.4, 122.8, 122.0, 35.2, 31.9; MS (EI) m/z: 315 $[M]^+$, 337 $[M + Na]^+$; anal. Calcd for $C_{24}H_{26}$: C, 91.67; H, 8.33. Found: C, 91.76; H, 8.20.

*2-(Adamant-1-yl)pyrene (**4**).* Purification by chromatography eluting with hexane/ethyl acetate (95/5, v/v) gave **4** [312 mg, 93% (Table 1, Entry 1)] as a white powder. mp 218−219 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.21 (s, 2H), 8.14 (d, J = 7.2 Hz, 2H), 8.07 (d, J = 9.0 Hz, 2H), 8.04 (d, J = 9.0 Hz, 2H), 7.96 (t, J = 7.2 Hz, 1H), 2.21 (s, 9H), 1.89 (s, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 149.2, 131.0, 131.0, 127.6, 127.1, 125.4, 124.6, 123.0, 121.9; MS (EI) m/z: 337 $[M]^+$, 359 $[M + Na]^+$; anal. Calcd for $C_{26}H_{24}$: C, 92.81; H, 7.19. Found: C, 92.67; H, 7.02.

*2,7-Di(adamant-1-yl)pyrene (**5**).* Purification by chromatography eluting with hexane/ethyl acetate (95/5, v/v) gave **5** [447 mg, 95% (Table 1, Entry 5)] as a white powder. mp > 300 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.17 (s, 4H), 8.03 (s, 4H), 2.21 (s, 18H), 1.89 (s, 12H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 148.8, 130.8, 127.4, 123.0, 121.6, 43.8, 36.9, 29.1; MS (EI) m/z: 471 $[M]^+$, 493 $[M + Na]^+$; anal. Calcd for $C_{36}H_{38}$: C, 91.86; H, 8.14. Found: C, 91.96; H, 8.01.

*1,3-Bis(pyren-2-yl)adamantane (**6**).* Purification by chromatography eluting with hexane/ethyl acetate (90/10, v/v) gave **6** [332 mg, 62% (Table 1, entry 8)] as a white powder. mp 274−275 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (s, 4H), 8.15 (d, J = 7.8 Hz, 4H), 8.09 (d, J = 9.0 Hz, 4H), 8.06 (d, J = 9.0 Hz, 4H), 7.96 (t, J = 7.8 Hz,

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2H), 2.11 (s, 2H), 2.57 (s, 2H), 2.36 (q, J = 12.0 Hz, 8H), 2.02 (s, 2H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 148.5, 131.1, 130.9, 127.6, 127.3, 125.5, 124.7, 124.6, 123.1, 121.9, 50.2, 43.0, 38.0, 36.1, 29.9; MS (EI) m/z: 537 $[M]^+$, 559 $[M + Na]^+$; anal. Calcd for $C_{42}H_{32}$: C, 93.89; H, 6.01. Found: C, 94.02; H, 5.88.

1,3,5-Tris(pyren-2-yl)adamantane (7). Purification by chromatography eluting with hexane/ethyl acetate (85/15, v/v) gave **7** [464 mg, 63% (Table 1, entry 10)] as a white powder. mp 221−222 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 8.42 (s, 6H), 8.17 (d, J = 7.8 Hz, 6H), 8.12 (d, J = 9.0 Hz, 6H), 8.08 (d, J = 9.0 Hz, 6H), 7.99 (t, J = 7.8 Hz, 3H), 2.86 (m, 1H), 2.82 (d, J = 12.0 Hz, 3H), 2.75 (d, J = 12.6 Hz, 3H), 2.48 (d, J = 2.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$): δ 147.8, 131.2, 131.0, 127.6, 127.4, 125.6, 124.8, 124.5, 123.3, 121.9, 49.4, 42.2, 39.2, 30.7; MS (EI) m/z: 737 $[M]^+$, 759 $[M + Na]^+$; anal. Calcd for $C_{58}H_{40}$: C, 94.53; H, 5.47. Found: C, 94.41; H, 5.35.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01060.

^1H and ^{13}C NMR spectra and absorption and emission spectra and photophysical data for compounds **2**−**7** (PDF)

Crystal structure data of compound **7** (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from the Polish National Science Centre (NCN, Grant Miniatura 2018/02/X/ST5/01472) is gratefully acknowledged.

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https://dx.doi.org/10.1021/acs.joc.0c01060
J. Org. Chem. 2020, 85, 11134−11139