Supplementary Information

Substitution Position Tuning the Different Aggregation-induced Emission Properties of Four (1-Naphthyl)vinyl(9-anthryl)vinylbenzene Isomers: from ACQ, AIEE to AIE

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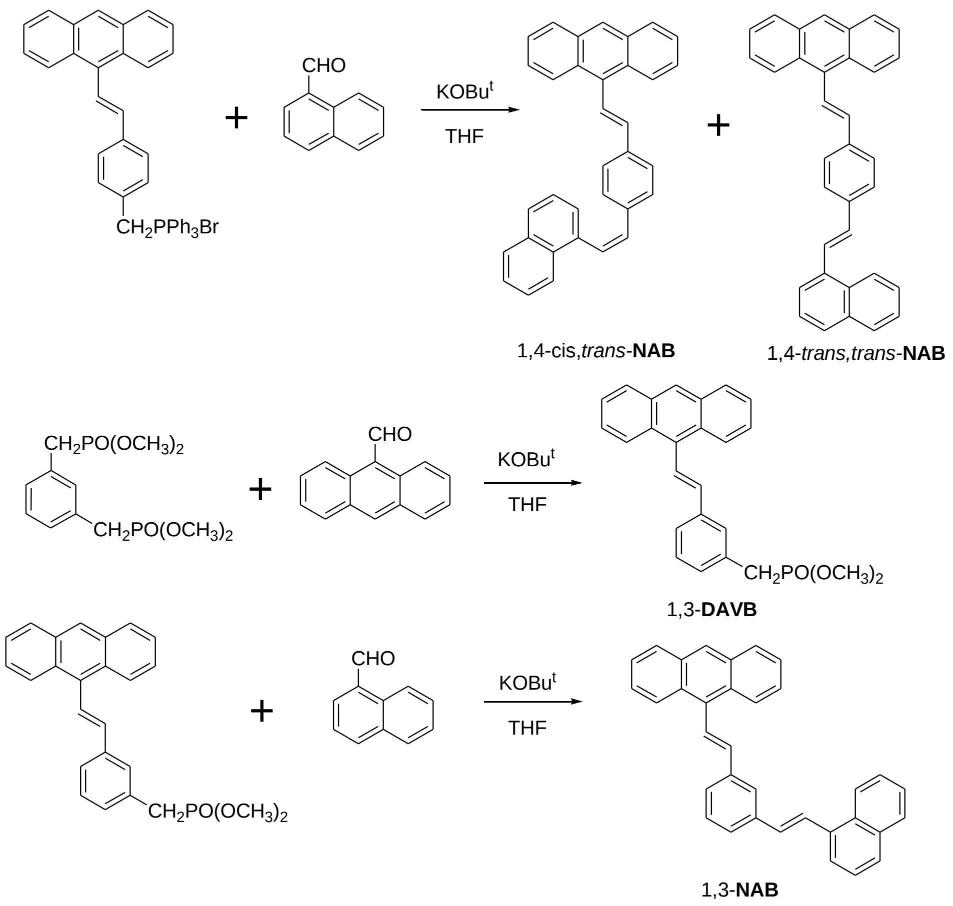
Experimental

Materials and Instrumentations

4-[(9-Anthryl)vinyl]benzyltriphenylphosphonium bromide were prepared according to the published procedures.[1] ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 or 400 spectrometer. Absorption measurements were carried out on a TU-1800 spectrophotometer. Photoluminescence (PL) measurements were recorded using a Hitachi F-4500 fluorescence spectrophotometer. Time-resolved emission decay behavior was recorded on an Endinburgh Instruments FLS920. The absolute photoluminescence quantum efficiency (Φ_F) values of the solid film and CH_2Cl_2 solution (10^{-5} M) were determined on an Endinburgh Instruments FLS920 using an integrating sphere. Elemental analyses were performed using a Perkin Elmer 2400II elemental analyzer. High-resolution mass spectral analyses were carried out on a Bruker maXis UHR-TOF mass spectrometer. Single-crystal X-ray diffraction measurements were conducted on an Oxford Diffraction Gemini E diffractometer. The structure was solved by direct methods and refined by a full-matrix least-squares technique on F^2 using SHELXL-97 programs.[2,3] CCDC-860990 (1,4-*cis*,*trans*-**NAB**) and CCDC-860992 (1,4-*trans*,*trans*-**NAB**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Scheme S1 Synthetic routes to 1,4-*cis*,*trans*-**NAB**, 1,4-*trans*,*trans*-**NAB** and 1,3-**NAB**.

Synthesis

*1-(1-Naphthyl)vinyl-4-(9-anthryl)vinylbenzene (1,4-**NAB**).* At room temperature, t-BuOK (0.07 g, 0.62 mmol) was added in batch into a mixture of 4-[(9-anthryl)vinyl]benzyltriphenylphosphonium bromide (0.19 g, 0.29 mmol) and 1-naphthylcarboxaldehyde (0.10 g, 0.64 mmol) in CH_2Cl_2 (20 mL) under nitrogen. After stirring overnight at room temperature, the mixture was poured into H_2O (40 mL) and extracted by CH_2Cl_2. The organic phase was combined and dried over $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel (petroleum ether) to afford two yellow solids, which were proved to be a pair of isomers. The first compound was 1,4-*cis*,*trans*-**NAB** (0.04 g, yield 30.8%), and the second one was 1,4-*trans*,*trans*-**NAB** (0.06 g, yield 46.2%).

1,4-*Cis*,*trans*-**NAB**: R_f = 0.35 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 6.83 (d, J = 16.5 Hz, 1H), 6.89 (d, J = 12.3 Hz, 1H), 7.11 (d, J = 12.3 Hz, 1H), 7.17 (d, J = 8.4 Hz, 2H), 7.39-7.48 (m, 8H), 7.51-7.55 (m, 2H), 7.80-7.85 (m, 2H), 7.89-7.92 (m, 1H), 7.98-8.01 (m, 2H), 8.11-8.15 (m, 1H), 8.27-8.30 (m, 2H), 8.38 (s, 1H). Elemental analysis calcd (%) for $C_{34}H_{24}$: C, 94.41; H, 5.59; found: C, 94.12; H, 5.16.

1,4-*Trans*,*trans*-**NAB**: R_f = 0.26 (petroleum ether/CH_2Cl_2 = 5:1). ^{1}H NMR ($CDCl_3$, 300 MHz) δ: 7.00 (d, J = 16.5 Hz, 1H), 7.23 (d, J = 16.5 Hz, 1H), 7.48-7.61 (m, 7H), 7.68-7.75 (m, 4H), 7.80-7.85 (m, 2H), 7.89-7.91 (m, 1H), 7.95 (d, J =3.0 Hz, 1H), 8.00-8.05 (m, 3H), 8.28 (d, J =8.1 Hz, 1H), 8.38-8.43 (m, 3H). ^{13}C NMR ($CDCl_3$, 75.47 MHz) δ: 123.13, 123.24, 124.43, 124.70, 125.02, 125.21, 125.37, 125.51, 125.65, 126.02, 126.50, 126.64, 127.64, 128.17, 128.22, 129.29, 130.79, 130.94, 131.06, 132.24, 133.31, 134.45, 136.34, 136.44, 136.94. Elemental analysis calcd (%) for $C_{34}H_{24}$: C, 94.41; H, 5.59; found: C, 93.80; H, 6.08.

1-Dimethoxyphosphorylmethyl-3-(9-anthryl)vinylbenzene. At room temperature, t-BuOK (1.18 g, 10.6 mmol) was added in batch into a mixture of 1,3-bis(dimethoxyphosphorylmethyl)benzene (3.10 g, 9.63 mmol) and 9-anthrylcarboxaldehyde (1.65 g, 8.01 mmol) in THF (30 mL) under nitrogen. After stirring overnight, the mixture was poured into H_2O (40 mL) and extracted by CH_2Cl_2. The organic phase was combined and dried over $MgSO_4$. After evaporation of the solvent, the crude product was chromatographed on silica gel (ethyl acetate) to afford a yellow solid (1.41 g, yield 43.8%).^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.26 (d, J = 21.6 Hz, 2H), 3.74 (d, J = 11.2 Hz, 6H), 6.94 (d, J = 16.4 Hz, 1H), 7.31 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.44-7.50 (m, 4H), 7.58-7.61 (m, 2H), 7.94 (d, J = 16.4 Hz, 1H), 8.01-8.03 (m, 2H), 8.34-8.36 (m, 2H), 8.42 (s, 1H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 33.29 (d, J = 138.8 Hz), 53.12 (d, J = 7.0 Hz), 125.32 (d, J =3.0 Hz), 125.47, 126.66, 126.13, 126.69, 128.20 (d, J = 7.0 Hz), 128.85, 129.26 (d, J = 3.0 Hz), 129.45

(d, *J* = 6.0 Hz), 129.86, 131.65, 132.04 (d, *J* = 9.0 Hz), 132.72, 137.08, 137.90 (d, *J* = 3.0 Hz). MS: *m/z* calcd for $C_{25}H_{24}O_3P$: 403.1 $[M+H]^+$; found: 403.1

1-Dimethoxyphosphorylmethyl-2-(9-anthryl)vinylbenzene. This compound was prepared from t-BuOK (0.54 g, 4.8 mmol), 9-anthrylcarboxaldehyde (0.75 g, 3.6 mmol) and 1,2-bis(dimethoxyphosphorylmethyl)benzene (1.4 g, 4.3 mmol) using the same procedure described for 3-dimethoxyphosphorylmethyl-2-(9-anthracenyl)vinylbenzene. The crude product was chromatographed on silica gel (ethyl acetate) to afford a yellow solid (0.46 g, yield 31.2%).^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.30 (d, *J* = 22.4 Hz, 2H), 3.72 (d, *J* = 10.8 Hz, 6H), 7.28 (d, *J* = 16.0 Hz, 1H), 7.34-7.37 (m, 1H), 7.40-7.44 (m, 2H), 7.46-7.54 (m, 4H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 8.02-8.04 (m, 2H), 8.39-8.43 (m, 3H). ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ: 30.29 (d, *J* = 137.8 Hz), 53.00 (d, *J* = 7.0 Hz), 125.34, 125.69, 126.05, 126.70 (d, *J* = 3.0 Hz), 126.78, 127.76, 127.84 (d, *J* = 3.0 Hz), 128.31 (d, *J* = 4.0 Hz), 128.87, 129.36 (d, *J* = 9.0 Hz), 129.86, 131.49 (d, *J* = 4.0 Hz), 131.63, 132.80, 135.07 (d, *J* = 42.0 Hz), 137.24 (d, *J* = 6.0 Hz). MS: *m/z* calcd for $C_{25}H_{24}O_3P$: 403.1 $[M+H]^+$; found: 403.1

*1-(1-Naphthyl)vinyl-3-(9-anthryl)vinylbenzene (1,3-**NAB**)*. This compound was prepared from t-BuOK (0.23 g, 2.0 mmol), 1-naphthylcarboxaldehyde (0.37 g, 2.4 mmol) and 1-dimethoxyphosphorylmethyl-3-(9-anthryl)vinylbenzene (0.40 g, 1.0 mmol) in THF (20 mL) using the similar procedure described for 1,4-**NAB**. The crude product was chromatographed on silica gel (petroleum ether) to afford a yellow solid (0.16 g, yield 37.0%). ^{1}H-NMR (400 MHz, [D6]acetone) δ: 7.07 (d, *J* = 16.4 Hz, 1H), 7.41 (d, *J* = 16.0 Hz, 1H), 7.52-7.58 (m, 8H), 7.76-7.79 (m, 2H), 7.88-7.96 (m, 3H), 8.11-8.13 (m, 2H), 8.21-8.28 (m, 3H), 8.42-8.47 (m, 3H), 8.56 (s, 1H). ^{13}C-NMR (100.6 MHz, [D6]acetone) δ: 124.27, 124.72, 125.93, 125.97, 126.19, 126.55, 126.67, 126.69, 126.77, 126.82, 127.03, 127.36, 127.53, 128.95, 129.44, 129.60, 130.10, 130.58, 132.37, 132.59, 133.64, 134.87, 135.79, 138.19, 138.74, 139.20. MS: *m/z* calcd for $C_{34}H_{25}$: 432.2 $[M+H]^+$; found: 432.2. Elemental analysis calcd (%) for $C_{34}H_{24}$: C, 94.41; H, 5.59; found: C, 94.77; H, 5.50.

*1-(1-Naphthyl)vinyl-2-(9-anthryl)vinylbenzene (1,2-**NAB**)*. This compound was prepared from t-BuOK (0.11 g, 0.98 mmol), 1-naphthylcarboxaldehyde (0.16 g, 1.0 mmol) and 1-dimethoxyphosphorylmethyl-2-(9-anthryl)vinylbenzene (0.20 g, 0.50 mmol) in THF (20 mL) using the same procedure described for 1,3-**NAB**. The crude product was chromatographed on silica gel (petroleum ether/CH_2Cl_2 = 10:1) to afford a yellow solid (0.10 g, yield 46.3%). ^{1}H-NMR (400 MHz, [D6]acetone) δ: 7.42-7.46 (m, 2H), 7.48-7.54 (m, 8H), 7.74 (d, J = 16.0 Hz, 1H), 7.81-7.90 (m, 3H), 7.95-8.02 (m, 3H), 8.07-8.11 (m, 3H), 8.31 (d, J = 8.4 Hz, 1H), 8.48-8.50 (m, 2H), 8.55 (s, 1H). ^{13}C-NMR(100.6 MHz, [D6]acetone) δ: 124.42, 124.60, 126.21, 126.60, 126.64, 126.72, 126.79, 127.05, 127.45, 127.94, 128.05, 128.45, 129.00, 129.03, 129.16, 129.29, 129.41, 129.62, 130.26, 130.63, 132.28, 132.63, 133.78, 134.81, 135.76, 136.75, 137.23, 137.28. MS: m/z calcd for $C_{34}H_{25}$: 432.2 $[M+H]^+$; found: 432.2. Elemental analysis calcd (%) for $C_{34}H_{24}$: C, 94.41; H, 5.59; found: C, 94.52; H, 5.90.

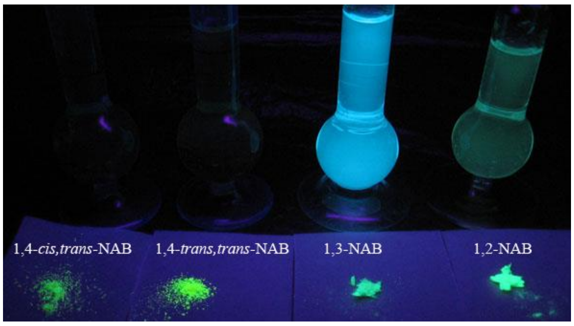


Fig. S1 Fluorescence image of the THF solutions (upper) and solids (lower) of compounds 1,4-*cis,trans*-**NAB**, 1,4-*trans,trans*-**NAB**, 1,3-**NAB** and 1,2-**NAB** under illumination with a 365.0 nm UV lamp.

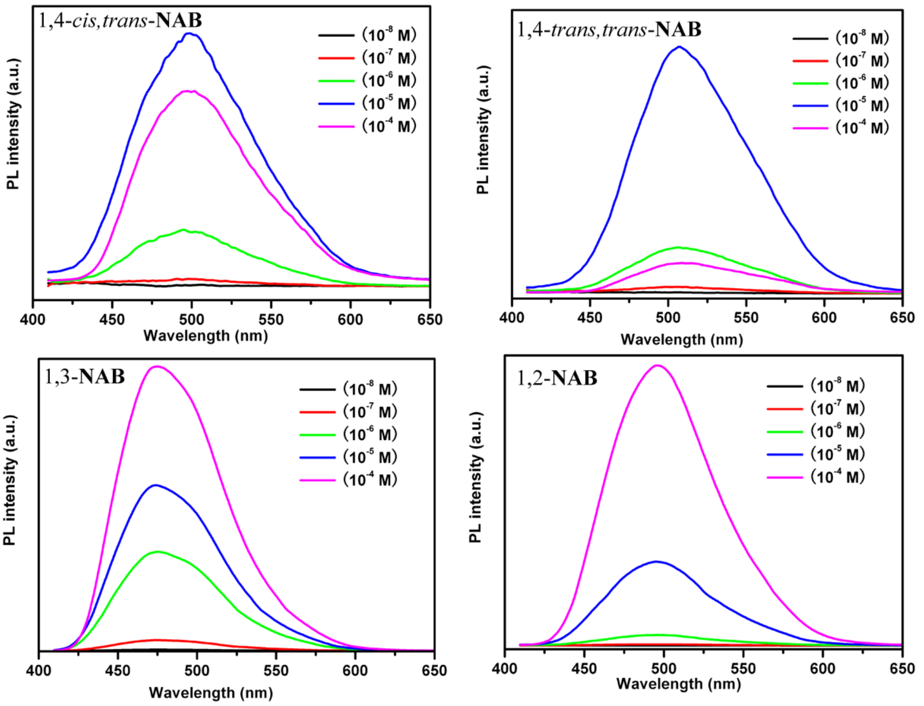


Fig. S2 Emission spectra in CH_2Cl_2 solutions with different concentrations. $\lambda_{ex} = 389$ nm.

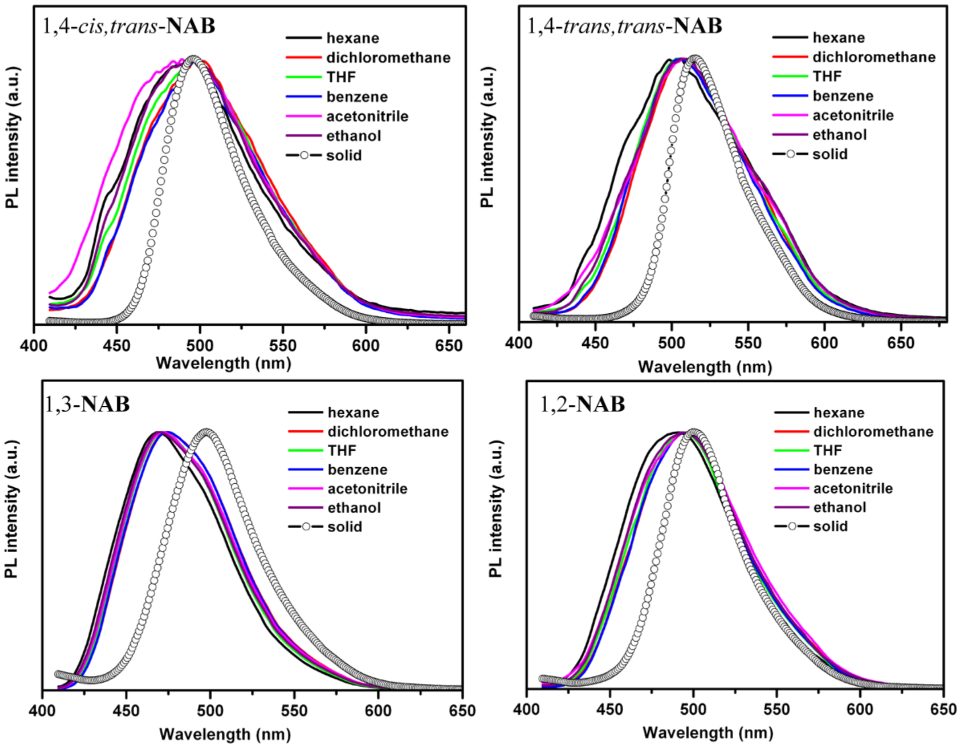


Fig. S3 Normalized emission spectra in solvents with different polarity (10^{-5} M) and as solid film. $\lambda_{ex} = 389$ nm.

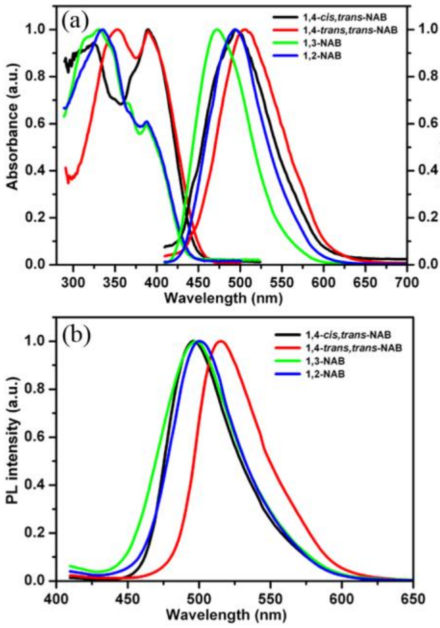


Fig. S4 (a) Normalized optical absorption and emission spectra in THF solution (10^{-5} M). (b) Normalized solid emission spectra. λ_{ex} = 389 nm.

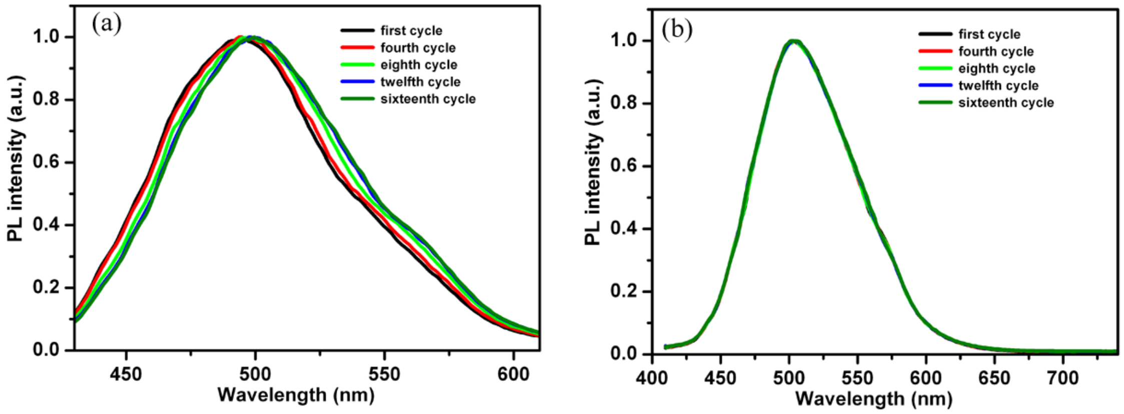


Fig. S5 The repeated scans of emission spectra in THF solution (10^{-4} M) at a rate of 240 nm/min from 409 to 750 nm: (a) 1,4-*cis*,*trans*-**NAB**; (b) 1,4-*trans*,*trans*-**NAB**. λ_{ex} = 389 nm.

Table S1 Crystal data and details of collection and refinement for 1,4-*cis,trans*-**NAB**, and 14,-*trans,trans*-**NAB**

Compound	1,4-*cis,trans*-**NAB**	14,-*trans,trans*-**NAB**
Chemical formula	$C_{34}H_{24}$	$C_{34}H_{24}$
Formula Mass	432.53	432.53
Crystal system	Monoclinic	Monoclinic
a/Å	16.850(4)	15.7869(7)
b/Å	6.4351(18)	6.0629(3)
c/Å	22.782(6)	25.6359(10)
α/°	90.00	90.00
β/°	107.41(3)	107.102(5)
γ/°	90.00	90.00
V/Å^3	2357.1(11)	2345.24(17)
Temperature/K	291.15	291.15
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
No. of reflections measured	12323	18229
No. of independent reflections	4787	4800
R_{int}	0.0706	0.0440
R_1 ($I > 2\sigma(I)$)	0.0718	0.0530
wR_2 ($I > 2\sigma(I)$)	0.1227	0.1104
R_1 (all data)	0.2100	0.0934
wR_2 (all data)	0.1774	0.1298
Goodness of fit on F^2	1.025	1.012

References

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